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THE ANALYLSIS OF IRON ORES CONTAINING BOTH PHOSPHORIC AND TITANIC ACIDS.[1]

BY THOMAS M. DROWN AND P. W. SHIMER.

The precipitation of phosphoric with titanic acid by boiling an iron solution which had been reduced to the ferrous condition by sulphuretted hydrogen or sulphurous acid was first noticed by E. H. Bogardus in 1874.[2] Since that time, as far as we are aware, not much has been published on the relation of these two acids to each other, and to silicic acid in the ordinary course of analysis of iron ores. The following investigation may perhaps aid in clearing up some of the obscure points in the analysis of titaniferous ores.

The Determination of Phosphorus.

From two to five grams of the finely powdered ore are weighed into a beaker and treated with about 50 cc. of hydrochloric acid (sp. gr. 1.12), evaporated to dryness, and heated in an air-bath for an hour to 110° to 120° C. To the dry mass are added 50 cc. of hydrochloric acid (1.12), and the solution filtered off from the insoluble residue. On washing this residue with water the filtrate often runs through turbid. This can be avoided by washing with dilute nitric acid, or, better, with an acid solution of ammonium

[1] Read before the American Institute of Mining Engineers.
[2] American Journal of Science, III. 8, 334.

nitrate. The filtrate contains the greater part of the phosphoric acid, but the residue may contain a notable amount.

Treatment of the Residue.—Fuse the residue with sodium carbonate and extract with water. Sodium phosphate and silicate go into solution and sodium titanate remains insoluble. Filter, acidify the filtrate with nitric acid, evaporate to dryness, moisten with nitric acid, and dissolve in water. Filter from the silica, concentrate the filtrate, neutralize nearly with ammonia, and precipitate with ammonium molybdate. This is the best method of separating the phosphorus from the insoluble residue. The bulk of the phosphorus may, however, be extracted from the moist residue by washing with ammonia.

Treatment of the Filtrate.—Evaporate to a small bulk, and add enough nitric acid to drive off all the hydrochloric acid on evaporation. If the concentrated solution is clear, add ammonia until a slight permanent precipitate is formed; redissolve this in a few drops of nitric acid, and add ammonium molybdate solution.

In the ores of which we are speaking, a precipitate generally separates on evaporating to a small bulk. The addition of more nitric acid with continued heat often redissolves this; in this case, the evaporation must not be carried too far, or the substance will again precipitate. This precipitate contains phosphoric acid and titanic acid. If it is impossible to get it into solution in nitric acid, it must be filtered off and washed with ammonium nitrate solution. It is then ignited, fused with sodium carbonate, extracted with water, and the filtrate, after acidifying with nitric acid, precipitated with molybdate solution.

After the addition of the ammonium molybdate to the main solution, as mentioned above, it is heated rather hot, say from 50° to 70° C., for half an hour, with frequent vigorous stirring. The precipitate is usually allowed to stand over night, but if filtered within two hours, there will be no appreciable amount of phosphorus unprecipitated. The yellow precipitate is filtered off and washed well with a mixture of 325 cc. of nitric acid (sp. gr. 1.2), 100 cc. of ammonium hydrate (sp. gr. 0.96), and 100 cc. of water. It is then dissolved upon the filter in dilute ammonia. The solution will probably run through turbid, and a gelatinous residue will remain in the filter. The solution is heated for some time and filtered, and this residue, which contains both phosphoric and titanic acid, is treated, together with the gelatinous residue insoluble in ammonia,

with nitric acid, and the resulting solution precipitated with ammonium molybdate. By heating and stirring, the phosphoric acid can be completely precipitated in an hour, so that it will not retard the analysis materially. The solution of this yellow precipitate in ammonia is to be added to the main ammoniacal solution, and magnesia mixture added with the usual precautions. By active stirring after the addition of magnesia mixture the complete precipitation of the phosphoric acid may be effected in an hour or two.[1] In the analysis of an ore containing 4.74 per cent. of phosphoric acid (mostly as apatite) and 0.65 per cent. of titanic acid, the phosphoric acid was found (in duplicate analyses) as follows:

	I.	II.
Phosphoric acid in the hydrochloric acid solution,	4.370	4.330
Phosphoric acid in the residue insoluble in hydrochloric acid,	0.280	0.390
Phosphoric acid in the precipitate which separated from the solution of the yellow precipitate in ammonium hydrate,	0.016	0.02
Total,	4.666	4.747

Determination of the Titanic Acid.

One to two grams of the finely powdered ore are weighed into a large platinum crucible. Potassium bisulphate[2] to the amount of 12 to 15 times the weight of the ore is next weighed out in another vessel. Mix the ore in the bottom of the crucible with about one-quarter of the bisulphate, and fuse until the excess of sulphuric acid is nearly all driven off. During the progress of the fusion, the lid must be lifted a very little at short intervals, in order to watch the state of the fusion. It should not be allowed to rise above two-thirds the height of the crucible. Add now another quarter of the bisulphate, and heat again as before, until nearly all the excess of the sulphuric acid is driven off. Then add the remaining half of the bisulphate, and heat until the whole mass is in

[1] The action of stirring or other agitation in hastening precipitation, although well known, is not, I think, as often made use of in analysis as it might be.

[2] In order to make a successful determination of titanic acid, it is necessary to have good potassium bisulphate. This can seldom be bought in a condition fit for use. It usually contains water; sometimes an excess of sulphuric acid; it also usually contains an insoluble siliceous residue. To prepare it for use, it is dissolved in water and filtered, the solution evaporated to dryness, and fused until all the water is driven off and the mass is in quiet fusion. It is sometimes necessary to drive off some sulphuric acid. It is then powdered for use. Bisulphate thus prepared will not mount readily in the crucible, and a quiet fusion at a red heat can be obtained.

quiet fusion. Too much sulphuric acid should not be driven off at this stage, or the subsequent solution in water will be retarded. The fused mass may be poured out into a large platinum dish, or it may be removed from the crucible in one lump by inserting a stout piece of platinum wire while still soft, and allowing the mass to solidify about it. A gentle heat on the outside of the crucible will quickly loosen the mass, which may now be lifted out easily. The former method is preferable, because of the thinness of the mass and its readier solubility.

When the mass has become cold, it is dissolved in plenty of cold water. This usually requires at least twelve hours. When it is evident that all has dissolved but silica and silicates,[1] filter into a large beaker. This insoluble residue should, after ignition, be again fused with bisulphate and tested as below for titanic acid. To the main solution we add sodium carbonate solution until a slight permanent precipitate is obtained, then 3 to 4 cc. of sulphuric acid of 1.23 sp. gr. This redissolves the slight precipitate and makes the solution sufficiently acid.

Add now sulphurous acid in excess, and dilute largely with water (1 to 1.5 liter); cover with a watch-glass, and boil about two hours, adding sulphurous acid solution and water as the evaporation goes on.

The titanic acid is precipitated, and with it phosphoric acid and oxide of iron. Filter hot (best done by means of a siphon), and wash with hot water. This precipitate of titanic acid and phosphoric acid is not finely granular like that of pure titanic acid, but is flocculent, and shows no tendency to run through even a very porous filter. It is dried, ignited, and weighed. In spite of the fact that it contains a very notable amount of iron, it is usually white after ignition. It is fused with sodium carbonate and extracted with water. Sodium titanate and oxide of iron remain insoluble, while sodium phosphate goes into solution. The residue is dissolved in sulphuric acid (sp. gr. 1.23), filtered, neutralized with sodium carbonate, 2 to 3 cc. of sulphuric acid added, and then sulphurous acid as above. The titanic acid precipitated from this solution is free from phosphoric acid and iron.

If, instead of fusing the first precipitate of titanic acid with sodium carbonate, it is re-fused with potassium bisulphate, there will remain on treatment with cold water an isoluble residue containing titanic acid and phosphoric acid.

[1] In ores containing lime, calcium sulphate is often found in this insoluble residue.

The following analytical results will illustrate the foregoing description:

	I.	II.
First precipitate of titanic acid containing phosphoric acid and iron (in duplicate), per cent.	3.18	2.40

No. 1 was fused with sodium carbonate and treated with water as above. It consisted of

Titanic acid, ...	0.65
Phosphoric acid, ...	1.60
Sesquioxide of iron, ...	.84
Loss, ...	.09
	3.18

No. 2 was fused with potassium bisulphate, and gave:

Residue insoluble in cold water, ...	1.83
Precipitate by boiling the solution, ...	.34
Sesquioxide of iron, by difference, ...	.23
	2.40

The titanic acid precipitated by boiling (.34) contained both phosphoric acid and iron.

The residue insoluble in cold water (1.83) was fused with sodium carbonate as described above; it gave:

Phosphoric acid, ...	.96
Titanic acid, ...	.42
Sesquioxide of iron, by difference, ...	.45
	1.83

The precipitate by boiling (.34), similarly treated, gave:

Phosphoric acid, ...	.05
Titanic acid, ...	.12
Sesquioxide of iron, by difference, ...	.17
	.34

The complete analysis of the original precipitate (2.40) thus shows:

Titanic acid, ...	.54
Phosphoric acid, ...	1.01
Sesquioxide of iron, by difference, ...	.85
	2.40

The titanic acid is here doubtless 10 per cent. too low, owing to the many fusions and precipitations to which it was subjected.

Determination of Iron.

If the ore contains less than one per cent. of titanic acid, no appreciable error will result from neglecting it. If it contains more than this, the iron must be determined in the filtrate from the titanic acid. The first precipitation of titanic acid contains iron. This is separated by the sodium carbonate fusion, and may be added to the main solution after separation of the titanic acid. The iron is then determined by reduction with zinc and titration with permanganate.

Determination of Silica and Alumina.

When an iron ore containing phosphoric and titanic acids is treated for silica by the usual method (fusion with sodium carbonate, solution in dilute hydrochloric acid, evaporation to dryness, and separation of silica at 110° C., solution in hydrochloric acid and water, and filtration from the insoluble residue), the siliceous residue consists of silica, titanic acid, phosphoric acid, and iron. In the case of an ore containing 3.50 per cent. of silica, this residue (which, in spite of the iron in it, is white after ignition) amounted to 6.11 per cent. The presence of phosphoric acid and iron with the silica of course renders worthless the estimation of alumina by difference.

Before speaking of the determination of the silica, we will consider how we may get the phosphoric acid and iron into the main solution where they belong. The insoluble residue (containing silica, titanic acid, phosphoric acid, and iron) is fused with sodium carbonate, and extracted with water. Sodium phosphate and silicate dissolve, and sodium titanate and ferric oxide remain behind. Acidify the filtrate with hydrochloric acid, and evaporate to dryness; take up with hydrochloric acid and water, and filter off the silica; add the filtrate to the solution to be precipitated by sodium acetate. Dissolve the residue insoluble in water (containing the sodium titanate and ferric oxide) in sulphuric acid, and separate the titanic acid from the iron by boiling, as usual. Filter from the titanic acid, and add bromine-water to the filtrate, in order to oxidize the iron, boil, and precipitate the iron with ammonia. Filter and weigh it with the precipitate of iron, alumina, and phosphoric acid, separated as basic acetate.

Some titanic acid may go into the filtrate, which is to be precipitated by sodium acetate. In this case it will contaminate the

precipitate of iron, alumina, and phosphoric acid. It is therefore necessary, after this precipitate has been weighed, to grind it in an agate mortar, and weigh out accurately as much of it as possible, fuse with potassium bisulphate, and determine the titanic acid in it by boiling, etc. The titanic acid thus found is to be deducted from the weight of the original precipitate. There will not in all cases be titanic acid in this precipitate, but it is not safe to omit testing for it.

The silica may also be determined by fusing the residue from the second bisulphate fusion for titanic acid with sodium carbonate, and separating the silica, as usual. Or it may be determined by fusing 1 to 1.5 gram of the ore with sodium carbonate, dissolving in hydrochloric acid, and adding an excess (50 cc.) of sulphuric acid (1.23), and evaporating until all the hydrochloric acid is driven off. This renders the silica insoluble. By now dissolving the ferric sulphate in a large excess of hydrochloric acid by aid of heat, everything goes into solution but the silica. When this point is reached, it is known by the absence of everything but transparent gelatinous silica floating in flocks in the clear solution. Calcium sulphate may contaminate the silica, if the ore contains much lime; but it does not look like gelatinous silica, and dissolves on dilution with water.

The following determinations illustrate the foregoing description:

	I.	II.
Insoluble in hydrochloric acid,	6.11 per cent.	5.38 per cent.

Fused with sodium carbonate and extracted with water, solution contained:

I.		II.	
Silica,	3.31	Silica,	3.63
Phosphoric acid,	1.03	Phosphoric acid,	.71

Residue contained:

I.		II.	
Titanic acid,	.65	Titanic acid,	.65
Sesquioxide of iron,	1.33	Sesquioxide of iron,	.58

Totals.	I.	II.
Silica,	3.31	3.63
Phosphoric acid,	1.03	.71
Titanic acid,	.65	.65
Sesquioxide of iron,	1.33	.58
	6.32	5.57

	I.	II.	III.
Silica made insoluble by sulphuric acid,	3.40	3.48	3.54
Silica from residue insoluble in bisulphate,	3.70	3.74	..
Residue insoluble in bisulphate,	4.91	5.03	..

THE CONDITION OF SULPHUR IN COAL, AND ITS RELATION TO COKING.[1]

By Thomas M. Drown.

At the meeting of the Institute in New York, in February, 1880,[2] I described a process of determining sulphur in metallic sulphides with especial reference to the determination of pyrites in coal. The process, as then described, is as follows: A solution of sodium hydrate, of 1.25 specific gravity, is saturated with bromine. If an excess of bromine is used it must be neutralized by the addition of a little more sodium hydrate. The pulverized mineral or coal is moistened with 25 cc. of this solution and heated, then hydrochloric acid is added cautiously to just acid reaction. This operation is repeated with another 25 cc. of the alkaline solution, and again rendered acid. The mixture should be kept hot. The contents of the beaker or dish are then evaporated to dryness to separate silica and taken up by dilute hydrochloric acid. The sulphuric acid is precipitated, with the usual precautions, by barium chloride. In the paper referred to, determinations by this process of sulphur in coal were given, which, although agreeing closely with one another, yet fall far short of the total sulphur in the coal, and the inference was that the sulphur not oxidized by the treatment with the bromine solution was an organic constituent of the coal, and could only be determined by a process which would oxidize the coal completely.

I am now able to give further results of the application of this process to the analysis of coal and coke. The object in view in this investigation was to determine, if possible, the effect of coking on the amount and condition of sulphur in the coal. Although the results in this regard are not as decisive as could be wished, yet many interesting facts have been noticed in the course of the work.

The coals used were from Pennsylvania and Virginia and will be simply designated by letters. Two series of experiments were

[1] Read before the American Institute of Mining Engineers.
[2] This Journal, **2**, 401; and Transactions of the American Institute of Mining Engineers, **8**, 569.

made. In the first the coke was made in the laboratory, in platinum crucibles; and in the second, "industrial coke," made in beehive ovens, was used.

In the first series the total sulphur was determined, by way of control, by fusion with alkaline carbonates and nitre; and in the second, by Eschka's method of heating the coal with calcined magnesia and sodium carbonate.

First Series.

COAL A.

Proximate Analysis.		Analysis of Ash.	
Moisture . .	0.75	Silica, . . .	47.74
Volatile matters, .	15.35	Alumina and oxide of iron,	34.17
Fixed carbon, .	66.10	Lime, . . .	7.61
Ash, ...	17.80	Magnesia, . .	0.98
		Sulphuric acid .	5.30
	100.00		95.80

The small quantity of ash used for this analysis is doubtless the cause of the imperfect result.

SULPHUR DETERMINATIONS IN COAL A.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
By Bromine Mixture.	In residue from I. by combustion in oxygen and absorption by solution of potassium permanganate.	In Ash from II. by fusion with sodium carbonate.	Total, sum of I., II., and III.	By direct combustion of coal in oxygen, and absorption by solution of potassium permanganate.	In Ash from V. by fusion with sodium carbonate.	Total, sum of V. and VI.	Total by fusion with sodium carbonate and nitrate.
1.660	0.640	0.040	2.340	1.983	0.203	2.186	1.940
1.640	0.520	0.043	2.203	1.768	0.329	2.097	1.980
1.670	0.563	0.026	2.259	1.942	0.212	2.154	

SULPHUR DETERMINATIONS IN COKE A.

1.073	0.747	0.065	1.885	1.287	0.477	1.764	..
1.180	0.666	0.062	1.908	1.290	0.494	1.784	..
1.180	0.627	0.045	1.852	..	..	..	..

COAL B.

Proximate Analysis.		Analysis of Ash.	
Moisture, . .	3.48	Silica, . . .	28.89
Volatile matters, .	25.55	Alumina and oxide of iron,	65.92
Fixed carbon, .	66.63	Lime, . . .	2.49
Ash, . . .	4.34	Magnesia, . .	0.57
		Sulphuric acid, .	2.02
	100.00		99.89

SULPHUR DETERMINATIONS IN COAL B.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
By Bromine Mixture.	In residue from I. by combustion in oxygen, and absorption by solution of potassium permanganate.	In Ash from II. by fusion with sodium carbonate.	Total, sum of I., II., and III.	By direct combustion of coal in oxygen, and absorption by solution of potassium permanganate.	In Ash from V. by fusion with sodium carbonate.	Total, sum of V. and VI.	Total by fusion with sodium carbonate and nitrate.
0.041	0.450	0.031	0.522	0.431	0.058	0.489	0.474
0.035	0.464	0.037	0.536	0.461	0.035	0.496	0.373
..	..	..	..	0.454	0.053	0.507	..

SULPHUR DETERMINATIONS IN COKE B.

0.034	0.406	0.060	0.500	0.429	0.087	0.516	0.495
0.056	0.400	0.063	0.519	0.441	0.080	0.521	0.536

COAL C.

Proximate Analysis.		Analysis of Ash.	
Moisture, . .	1.16	Silica, . . .	60.94
Volatile matters, .	33.08	Alumina and oxide of iron,	32.86
Fixed carbon, .	61.81	Lime, . . .	1.75
Ash, . . .	3.95	Magnesia, . .	0.10
		Sulphuric acid, .	2.28
	100.00		97.93

SULPHUR DETERMINATIONS IN COAL C.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
By Bromine Mixture.	In residue from I. by combustion in oxygen, and absorption by solution of potassium permanganate.	In Ash from II. by fusion with sodium carbonate.	Total, sum of I., II., and III.	By direct combustion of coal in oxygen, and absorption by solution of potassium permanganate.	In Ash from V. by fusion with sodium carbonate.	Total, sum of V. and VI.	Total by fusion with sodium carbonate and nitrate.
0.127	0.647	0.028	0.802	0.693	0.036	0.729	0.766
0.139	0.631	0.022	0.792	0.701	0.030	0.731	0.712
..	..	.	..	0.762	0.035	0.797	..

SULPHUR DETERMINATIONS IN COKE C.

0.041	0.547	0.026	0.614	0.583	0.033	0.616	0.640
0.018	0.582	0.028	0.628	0.605	0.034	0.639	0.650

It has been recently stated by Mixter[1] that bromine-water, or a solution of bromine in hydrochloric acid, fails to oxidize all the sulphur dioxide produced by the combustion of coal, and that the vapors should be carried into a large bottle containing bromine vapors before they are allowed to escape. I have found also that a final large bromine bottle collects a very small amount of sulphuric acid after the vapors have passed through a solution of potassium permanganate. A coal containing 0.721 per cent. of sulphur gave 0.009 per cent. in the large bromine bottle, and another coal containing 0.605 per cent. gave 0.024 per cent. In the following experiments the large bromine bottle was used, and the sulphur given as absorbed by permanganate solution includes the small amount found in the bromine bottle. As stated in a previous paper, I much prefer potassium permanganate to bromine for the oxidation of sulphur dioxide or sulphuretted hydrogen.

In the combustion of bituminous coals in oxygen explosions frequently occur. These may be avoided by simply diluting the oxygen with atmospheric air to the extent of equal volumes. The coal or coke can be best ignited in the tube in the following manner. The platinum boat containing the coal is placed just within the tube,

[1] This Journal, 2, 396.

which is then filled with oxygen. The cork is then removed, and a glowing splinter of charcoal placed in the end of the boat, which is quickly pushed in the middle of the tube. The flow of oxygen is at once resumed and the coal continues to glow until it is all consumed. The gas in the combustion-furnace is kept turned low until the coal is nearly consumed, when it is turned on to a good red heat.

In the foregoing experiments the coke was made in platinum crucibles over a Bunsen burner. To test the effect of coking on an industrial scale, I had samples taken of the coal which was put into an oven and of the coke which came out. This was not done under my supervision, and consequently some uncertainty exists as to the thoroughness of the sampling. The following are the results obtained on three samples of coal and the corresponding coke made in ovens.

The total sulphur was directly determined in these coals and cokes by Eschka's method of heating with calcined magnesia and sodium carbonate, and oxidizing the solution in water by bromine. This is much to be preferred, in regard to simplicity and accuracy, to fusion with alkaline carbonates and nitre.

Second Series.

COAL E.

Proximate Analysis.

Volatile matters (including moisture),	24.25
Fixed carbon,	70.51
Ash,	5.24
	100.00
Ash in coke,	5.41

The ash determinations in this coal and coke indicate imperfect sampling.

SULPHUR DETERMINATIONS IN COAL E.

I. By Bromine Mixture.	II. In residue from I. by combustion in oxygen.	III. In Ash from II.	IV. Total.	V. Direct combustion in oxygen.	VI. In Ash from V.	VII. Total.	VIII. Total by Eschka's method.	IX. Iron.
0.155	0.488	0.020	0.663	0.721	0.044	0.765	0.733	0.32
0.156	0.478	0.017	0.651	0.679	0.032	0.711	..	..

SULPHUR DETERMINATIONS IN COKE E.

0.119	0.532	0.012	0.663	0.637	0.021	0.658	0.665	..
0.125	0.533	0.013	0.671	0.669	0.017	0.686	..	..

COAL F.

Proximate Analysis.

Volatile matters (including moisture), . . .	29.75
Fixed carbon, ...	62.37
Ash, ...	7.88
	100.00
Ash in coke, ...	9.80

SULPHUR DETERMINATIONS IN COAL F.

I. By Bromine Mixture.	II. In residue from I. by combustion in oxygen.	III. In Ash from II.	IV. Total.	V. Direct combustion in oxygen.	VI. In Ash.	VII. Total.	VIII. Total by Eschka's method.	IX. Iron.
0.349	0.560	0.014	0.923	0.923	0.045	0.968	0.949	0.666
0.354	0.546	0.012	0.912	0.905	0.043	0.948	..	..

SULPHUR DETERMINATIONS IN COKE F.

0.296	0.619	0.012	0.927	0.907	0.017	0.924	0.917	..
0.299	0.607	0.008	0.914	0.913	0.024	0.937	..	..

COAL G.

Proximate Analysis.

Volatile matters (including moisture),	38.01
Fixed carbon,	56.27
Ash,	5.72
	100.00
Ash in coke,	8.76

SULPHUR DETERMINATIONS IN COAL G.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
By Bromine Mixture.	In residue from I. by combustion in oxygen.	In Ash from II.	Total.	Direct combustion in oxygen.	In Ash from V.	Total.	Total by Eschka's method.	Iron.
0.129	0.588	0.018	0.735	0.749	0.042	0.791	0.759	0.290
..	..	..	..	0.727	0.045	0.772	..	..

SULPHUR DETERMINATIONS IN COKE G.

0.085	0.516	0.025	0.626	0.581	0.050	0.631	0.597	..
..	..	..	..	0.605	0.016	0.621	0.590	..

I add an analysis of anthracite, illustrating this method of treatment.

ANTHRACITE.

Analysis of Ash. (5.11 *per cent.*)

Silica,	50.06
Alumina and Iron,	44.22
Lime,	1.39
Magnesia,	0.21
Sulphuric acid,	2.05
	97.93

SULPHUR DETERMINATIONS IN ANTHRACITE.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
By Bromine Mixture.	In residue from I, by combustion in oxygen.	In Ash from II.	Total.	Direct combustion in oxygen.	In Ash from V.	Total.	Total by fusion with sodium carbonate and nitrate.
0.08	0.485	0.024	0.589	0.512	0.042	0.554	0.589
..	..	..	..	0.534	0.040	0.574	..

No calcium sulphate was found in any of these coals. They were tested by boiling for some time the finely pulverized coal with water slightly acidulated with hydrochloric acid, in a flask from which the air was excluded by a current of carbon dioxide. The precaution of excluding the air is necessary, since pulverized iron pyrites boiled with water (or solution of sodium carbonate, as has been recommended for the determination of calcium sulphate) with access of air is readily oxidized, and the water reacts for sulphuric acid.

In the second series of analyses it will be seen that there is in each case an excess of total sulphur over what is necessary to form pyrites with the iron, and that there is not enough sulphur, as determined by bromine, to form pyrites with all the iron. This would seem to indicate that the sulphur is present in these coals, both as pyrites and as an organic constituent of the coal, and also that the iron is present, both in combination with the sulphur and with silica or other inorganic constituents of the ash.

The foregoing determinations, while they are insufficient to throw much light on the effect of coking on the condition, or the elimination of sulphur in coal, may not be without value in indicating a new line of investigation of coals and cokes.

In the coal A, which contains sulphur in considerable amount, both as metallic sulphide and as an inherent constituent of the coal, and which, at the same time, is low in volatile ingredients, it would seem as if the elimination of sulphur was limited to a

portion of that existing as pyrites, and that the organic sulphur, if we may so call it, was not affected by the process of coking. This becomes apparent if the percentage of sulphur in the coke is calculated on the basis of the amount of coal required to make the coke.

In the other coals, low in pyrites and higher in volatile matters, there was an elimination of the organic surphur to the extent of 20 to 45 per cent. It would be interesting to determine the effect of different methods of coking, and of the duration of the process on this elimination.

If we admit the presence of organic sulphur in coke, it is probable that no plan for its removal could be effective which would not involve the destruction of the coke itself. In the method of analysis given, we are able to distinguish between the organic and inorganic combinations of sulphur in coke, and thus to determine the feasibility of its desulphurization.

It is interesting to note (more especially in coal A) that the ash of the coal which has been burned directly in oxygen contains much more sulphur than that from the same coal which has had its sulphur, in the form of pyrites, removed by bromine.

The analytical determinations in this investigation were made with great care by Mr. P. W. Shimer.

ON THE COMPOSITION OF AMERICAN GRASSES.

By Clifford Richardson.

The large number of analyses of grasses which have been made during the last few years in the laboratory of the Department of Agriculture make it possible to deduce certain averages for their composition which are of great interest, both in comparison with those of Wolff for German grasses, and as showing the relations of cultivated and wild grasses toward each other, and the variations in composition which one species may present when grown on different soils and in different climates.

In the following tables are presented the figures which I have obtained:

TABLE I.

AVERAGE COMPOSITION OF GRASSES IN BLOOM.

	AMERICAN.				GERMAN.		
	77 Analyses of Wild Grass.	21 Analyses of Grasses from one farm in Penn.	19 Analyses of Grasses from Dept. Grounds.	6 Analyses of Orchard Grass from Various Localities.	Wolff's Averages.		
					Fair.	Good.	Very Good.
Ash.....	7.90	7.95	7.44	7.38	6.30	7.23	8.24
Fat.....	2.90	3.12	3.52	3.33	2.34	2.92	3.29
N free Extract....	53.90	55.75	55.82	55.17	46.53	47.84	48.93
Crude Fibre	27.10	23.14	22.47	25.19	34.09	30.69	25.77
Nitrogen × 6.25..	8.20	10.04	10.25	8.91	10.74	11.32	13.77
P. c. N as Nonalb..	34.7	30.1	18.3	25.2	..	..	..
Nutritive Ratio...	1 : 10.2	1 : 8.1	1 : 8.0	1 : 9.4	1 : 7.7	1 : 7.2	1 : 5.7

It is plainly shown that all our American grasses are strikingly different in composition from similar German varieties. In the first place the content of nitrogen is smaller, accompanied by a largely decreased amount of fibre. In the next place, these changes are made up by a larger amount of nitrogen free extract and a slight increase in fat. The nutritive ratio, then, is much wider than in the German grasses.

Considering the relations of the different kinds of American grasses to each other, it is apparent that the wild varieties are, as would be expected, of much less nutritive value than those which have been cultivated. The average composition of orchard grass is not equal to that of the better cultivated varieties; and among the latter, the higher the cultivation the better the quality, as is shown by the averages for the grasses grown in Pennsylvania, which had not been as highly fertilized as those from the grounds of the Department of Agriculture in Washington. The explanation of the differences between American and German grasses may be that

the latter have been under cultivation so much longer that they have improved in quality; or rather, perhaps, that they grow on more highly fertilized soils from which they are able to assimilate larger amounts of nitrogen; the grasses, as is well known, being quite dependent on the soil for that element, while they are, owing to their larger content of fibre, perhaps of less real value than the American species. In this connection it would be most interesting to study the effect of different fertilizers on our native and cultivated species, and such a course of experiment I intend to carry out in the near future. Another prominent fact which is shown by the table is, that in the wild grasses the amount of nitrogen in the non-albuminoid form is larger than in the better varieties, and that the amount varies somewhat as the quality of the grass, the more highly cultivated varieties from the grounds of the Agricultural Department having only a little more than half as much as is found in the wild species. The character of the soils upon which the specimens grew which I have analyzed may have had some influence upon the results, outside of the amount of cultivation to which they were subjected. The wild grasses were for the greater part from the sandy soils of the South; those from Pennsylvania grew upon a micaceous loam, and the soil of the grounds of the Department of Agriculture is of a heavy nature, as indicated by an analysis in the report for 1879, p. 93.

In this connection the variations in the composition of a single species when grown in different localities is of interest, and in Table II. may be seen the changes which have been observed in *Dactylis.*

TABLE II.

ANALYSES OF *Dactylis Glomerata* [ORCHARD GRASS] FROM VARIOUS LOCALITIES.

EARLY BLOOM.

LOCALITY.	Ash.	Fat.	N. Free Extract.	Crude Fibre.	Nitrogen × 6.25.	Total Nitrogen.	Non-albuminoid Nitrogen.	Per cent. of Total N. as Non-alb.
District of Columbia	8.64	3.98	50.20	24.67	12.51	1.99	.70	38.7
North Carolina	8.90	3.68	52.16	24.97	10.29	1.61	.63	39.1

FULL BLOOM.

	Ash.	Fat.	N. Free Extract.	Crude Fibre.	Nitrogen × 6.25.	Total Nitrogen.	Non albuminoid Nitrogen.	Per cent. of Total Nit. as Non-alb.
North Carolina	7.42	3.56	56.03	23.08	9.91	1.58	.30	19.0
District of Columbia	8.07	3.24	53.76	25.40	9.53	1.53	.16	10.5
Maine	8.02	3.39	54.80	26.05	8.74	1.40	.36	25.7
District of Columbia	6.00	3.62	57.34	24.42	8.62	1.38	.42	30.4
Pennsylvania	6.33	2.66	54.94	28.51	8.56	1.37	.51	37.2
New Hampshire	8.44	3.49	54.75	24.91	8.41	1.35	.42	30.9
Average Early Bloom	8.77	3.83	51.18	24.82	11.40	1.80	.70	39.9
Average Full Bloom	7.38	3.33	55.19	25.19	8.91	1.43	.36	25.2

The specimens from the District of Columbia grew on a rather heavy soil similar to that before mentioned; those from North Carolina, on a light sandy soil; that from Maine, on a light loam; that from Pennsylvania, on a micaceous loam, and that from New Hampshire on a poor, loose loam; without much cultivation in any case, except the first two specimens in early and full bloom, from the District of Columbia and North Carolina.

Among these results it appears again strikingly that the amount of non-albuminoid nitrogen does not increase with an increase in the total amount of nitrogen in the grass, the poorer specimens having more than twice as much relatively to the total nitrogen than the more highly cultivated ones, owing to the fact that the absolute amount of non-albuminoid nitrogen does not vary within certain limits, the diminution of the total amount falling largely on the albuminoid forms. The variations in the non-nitrogenous elements of the plant do not show any regularity dependent on climate or surroundings, in the same way that the nitrogenous constituents do; and it is probable that a much larger number of analyses would be necessary to permit the drawing of conclusions in this direction.

The presence of non-albuminoid nitrogen in varying amount has been noted in the previous tables. In the following series of analyses of *Alopecurus pratensis*, Meadow Foxtail, which have been selected from a large series published in the report of the Department of Agriculture for 1880, the changes which

take place in its relative amount, as well as those of the general constituents of the plant, are shown.

TABLE III.

ANALYSES OF *Alopecurus Pratensis* AT FOUR STAGES OF GROWTH.

CONSTITUENTS.	HEAD APPEARING.		BEFORE BLOOM.		IN BLOOM.		AFTER BLOOM.	
When cut	April	19th.	April	19th.	May	1st.	May	12th.
Water in fresh grass	77.1	..	76.7	..	60.0	..	60.6	..
AIR DRY SUBSTANCE.								
Water	8.75	8.75	9.83	9.83	7.70	7.70	8.58	8.58
Ash	8.40	8.40	7.12	7.12	7.15	7.15	7.47	7.47
Ether Extract	4.28	..	4.02	..	3.10	..	3.20	..
Soluble in Alcohol	..	3.40	..	3.07	..	2.25	..	2.35
Insoluble in Alcohol	..	.88	..	.95	..	.85	..	.85
80 per cent. Alcohol Extract	16.36	..	12.63	..	11.65	..	10.20	..
Insoluble in Water	..	1.46	..	1.75	..	1.53	..	1.24
Soluble in Water	..	..	..	..	..	..	..	..
Sugars	..	3.40	..	2.40	..	2.70	.	2.70
Organic Acids, &c	..	8.67	..	5.28	.	7.42	..	5.98
Amido Bodies	..	2.83	..	2.26	..	.00	..	.28
Water Extract	3.02	3.02	2.06	2.06	1.68	1.68	1.64	1.64
Acid Extract	15.70	15.70	20.50	20.50	21.60	21.60	20.50	20.50
Alkali Extract (Diff.)	16.24	16.24	15.33	15.33	15.19	15.19	17.74	17.74
Crude Fibre	16.62	16.62	20.20	20.20	21.95	21.95	23.18	23.18
Albumen	10.63	10.63	9.25	9.25	9.98	9.98	7.49	7.49
DRY SUBSTANCE.								
Ash	9.21	9.21	7.90	7.90	7.75	7.75	8.17	8.17
Ether Extract	4.69	..	4.46	..	3.36	..	3.50	..
Soluble in Alcohol	..	3.73	..	3.40	..	2.44	..	2.57
Insoluble in Alcohol	..	.96	..	1.05	..	.92	..	.93
N. Free Extract	52.16	..	51.66	..	54.30	..	54.35	..
80 per. cent. Alcohol Extract	..	..	..	..	..	..	..	..
Insoluble in Water	..	1.60	..	1.94	..	1.65	..	1.36
Soluble in Water	..	..	..	..	..	..	..	..
Sugars	..	3.73	..	2.66	..	2.92	..	2.95
Organic Acids, &c	..	9.50	..	5.86	..	8.04	..	6.54
Amido Bodies	..	3.10	..	2.50	..	.00	..	.34
Water Extract	..	3.31	..	2.28	..	1.82	..	1.79
Acid Extract	..	17.20	..	22.74	..	23.41	..	22.42
Alkali Extract (Diff.)	..	6.79	..	17.00	..	16.46	..	19.41
Crude Fibre	18.21	18.21	22.41	22.41	23.78	23.78	25.36	25.36
Albumen	..	11.76	..	10.26	..	10.81	..	8.19
Nitrogen X 6.25	15.73	..	13.53	..	10.81	..	8.62	..
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Total Nitrogen	2.52	..	2.17	..	1.73	..	1.33	..
N. as Albumen	1.86	..	1.64	..	1.73	..	1.26	..
N. as Non-Albuminoid	.66	..	8.53	..	.00	..	.07	..
Per cent. of N. as Non-Albumin'd	38.2	..	40.9	..	0.0	..	5.0	..
Nutritive Ratio	1 : 4.8	..	1 : 5.8	..	1 : 7.5	..	1 : 9.7	..

In this grass, which may be regarded as typical of most cultivated grasses, the changes which take place during its growth are represented in a short series of analyses, as it matures in a few weeks. The total nitrogen diminishes regularly from early to late stages. The albumen diminishes nearly in the same way, but remains constant for quite a long period at the time of blooming.

The non-albuminoid nitrogenous substances, while decreasing rapidly from the first stage at which the grass was collected to nothing at full bloom, increase again slightly after bloom. In many other grasses which I have analyzed this increase is much larger, and is very apparent. Among the non-nitrogenous constituents the fibre increases toward maturity while the fat decreases. Those substances which make up what is known as the "nitrogen free extract" in fodder analyses, while they do not present the same regularity of change as the previously mentioned constituents, show, in a few instances, a regular diminution or increase toward maturity. The sugars, or those substances extracted by alcohol and not precipitated by basic lead acetate, which reduce Fehling's solution, do not vary largely, but there is a larger amount in the young plant than in the other stages, contrary to what has been found in the sugar-producing grasses, sorghum and sugar cane. The organic acids, too, are present in larger amount in the young plant. A regular diminution takes place in the amount of gum, and a somewhat irregular increase in those indefinite substances extracted by acid and alkali. The conclusions which can be drawn from these results are perhaps better suited to an agricultural paper, and they will be passed over here.

In what forms the nitrogen of the grasses exists it is not possible at present to decide, but the following determinations, made with a specimen of *Dactylis glomerata* in one of the earlier stages of its growth, before the development of the panicle, gives some idea of what may be sought for.

TABLE IV.

Dactylis Glomerata BEFORE THE APPEARANCE OF PANICLE.

Forms of Nitrogen.		
"Total nitrogen" (by soda lime)	2.40	2.38
N. soluble in water	.98	..
Soluble in 80 per cent. alcohol	.98	..
N. soluble in water and not precipitated by—		
tannic acid	.98	..
phosphotungstic acid	1.01	1.01
cupric hydrate	.84	.87
phosphomolybdic acid	.84	..
basic lead acetate	.84	.70
N. soluble in water and lactic acid and not precipitated by cupric hydrate	.73	.70
Nitric acid containing N	.099	..
Ammonia containing N	.093	..
Nitrogen as amides of amido acids	none.	

The forms of nitrogen which might occur in grasses are ammonia salts, nitrates, albumen, peptones, amides, amido-acids, alkaloids and carbamide bodies. The presence of albumen, ammonia salts and nitrates is shown by direct determination. The absence of alkaloids and peptones is shown by the fact that phosphotungstic and tannic acids do not precipitate anything from the water solution of the plant. That there are substances present in the water solution of the grass which are not precipitated by any of the reagents in the above table, points to the presence of amides or amido-acids. That the former are not present is shown by the fact that on boiling the aqueous extract with acids and then distilling with magnesia, no more ammonia is found than before the treatment with acid. The conclusion must be, then, that the non-albuminoid nitrogen of the plant exists as amido-acids, but of different kinds, as the different reagents do not all act uniformly in precipitating them, that is to say there is a substance precipitated by cupric hydrate which is not precipitated by tannic acid and phosphotungstate. It is probably an amido-acid forming difficultly soluble copper salts. Attempts to extract these nitrogenous bodies from a large amount of juice expressed from this grass were unsuccessful, owing to the presence of substances preventing crystallization.

WASHINGTON, *Dec.* 1881.

Contributions from the Chemical Laboratory of Harvard College.

XV.—AN INDIRECT DETERMINATION OF CHLORINE AND BROMINE BY ELECTROLYSIS.

BY LEONARD P. KINNICUTT.

In the indirect determination of chlorine and bromine the method most commonly employed is to precipitate both halogens with argentic nitrate, and then either to reduce the weighed argentic chloride and bromide to metallic silver by heating in an atmosphere of hydrogen, or to change the bromide into chloride by heating in a stream of chlorine gas.

The determination by either method is difficult, requires the closest attention, and is liable to give erroneous results; both on account of the slight loss that may occur in transferring the weighed chloride and bromide from the crucible to the glass tube, and also from slight volatilization during the heating. I have found that even in reducing the mixed haloids to metallic silver in a slow current of hydrogen, small particles of silver are almost always carried by the gas along the tube. Led by these facts, I attempted during the past winter to find a new method which would, if possible. from its accuracy and simplicity, tend to bring the indirect determination of chlorine and bromine when they occur in organic compounds more into vogue than is at present the case. In this attempt I believe I have been successful, and the method I have devised is based on the principle that melted argentic chloride and bromide are easily reduced to metallic silver by the galvanic current.

The details of the process are as follows:

After the mixture of the two halogen compounds of silver has been heated in a porcelain crucible so that they just fuse together, the crucible is cooled and weighed, a piece of platinum foil connected with a platinum wire is placed in the crucible so that it rests on the melted silver salts, and dilute sulphuric acid (1 pt. conc. to 3 pts. water by volume) is poured into the crucible until it is two-thirds full, a second piece of platinum foil united to a wire is then placed in the acid solution, care being taken that it does not touch the silver mixture. The zinc pole of a two-cell Bunsen battery is connected with the platinum foil that rests on the silver salts, and the carbon foil with the platinum foil just mentioned. The decomposition begins immediately, chlorine and bromine being given off from the positive electrode, the reduced silver remaining at the bottom of the crucible in the form of a porous mass. The reaction requires from twelve to eighteen hours; with a weight of less than one and a half gram of the mixed haloids I have found twelve hours sufficient to produce complete reduction; with a weight exceeding that amount I prefer to allow eighteen. When the argentic chloride and bromide are completely reduced, the battery is disconnected, the electrodes taken out of the sulphuric acid solution and washed with distilled water. The sulphuric is then poured off from the silver, and the silver is washed by decantation with distilled water, the decanted liquid being poured through a small

filter; this is afterwards burnt, added to the silver sponge which still remains in the crucible; the crucible is then heated over a low free flame to constant weight. The weight thus found, minus the weight of crucible and filter ash, is of course the weight of silver contained in the argentic chloride and bromide.

The only point that requires any great degree of care in this process is the melting of the mixed haloids. The temperature at which the fusion takes place must be as low as possible, so as to avoid any volatilization, and the melted mass should be united as far as practicable in one piece.

In some of the following analyses I have used a platinum crucible. When this has been the case, one wire has been wound around the crucible, while the other, as before, has been merely allowed to dip into the acid solution; in this way the whole crucible serves as an electrode, and there is no need of bringing the melted chloride and bromide into one globule. With a platinum crucible, the washing of the reduced silver must be continued until a few drops of the filtrate gives no precipitate with baric chloride, and the drying should be done in an air bath at a temperature of about 150° C. After weighing, the silver, which always adheres to the crucible, can be dissolved out with dilute nitric acid.

The first series of analyses shows the accuracy of the process when either argentic chloride or bromide is taken alone, the second series when they occur together.

First Series of Analyses.

Wt. taken. Argentic chloride.	Wt. found. Silver.	Wt. calculated. Silver.
0.7206 grams.	0.5419 grams.	0.5425 grams.
1.2984 "	0.9771 "	0.9777 "
1.8455 "	1.3892 "	1.3889 "

Wt. taken. Argentic bromide.	Wt. found. Silver.	Wt. calculated. Silver.
0.9313 grams.	0.5352 grams.	9.5350 grams.
0.9421 "	0.5424 "	0.5424 "

In this connection I publish, by permission, three analyses, made according to this process, by Prof. J. P. Cooke, in determining the purity of a sample of argentic bromide.

Wt. of argentic bromide.	Wt. of silver.	Per cent. of silver.
1. 4.1450 grams.	2.3817 grams.	57.444
2. 1.8172 "	1.0437 "	57.434
3. 4.9601 "	2.8497 "	57.449
Mean value		57.442

Second Series of Analyses.

Wt. taken. Argentic bromide.	Wt. taken. Argentic chloride.	Wt. taken. Silver.	Wt. calculated. Silver.
0.9389 gram.	1.0498 gram.	1.3283 gram.	1.3293 gr.
1.0915 "	1.3042 "	1.6095 "	1.6086 "
1.1779 "	1.2551 "	1.6229 "	1.6217 "
1.2470 "	1.5420 "	1.8778 "	1.8770 "
1.6153 "	0.6661 "	0.8560 "	0.8550 "

The slight increase of variation between the found and calculated results in this second series of analyses I attribute to a slight volatilization of the argentic chloride before the bromide undergoes fusion.

With the argentic iodide I have only tried qualitative experiments, but I can see no reason why its determination when mixed with either argentic chloride or bromide cannot be accomplished according to this method.

XVI.—THE DECOMPOSITION OF PHENYLTRIBROMPROPIONIC ACID BY WATER.

By Leonard P. Kinnicutt.

Glaser in his study of the addition products of cinnamic acid obtained two isomeric phenyltribrompropionic acids, and observed that they were decomposed by boiling water.[1] The nature or constitution of the substances was not investigated. In the hope that one of the products of this decomposition might be a phenylmonobromglyceric acid, the result of a reaction analogous

[1] Annalen der Chemie, **143**, 335 and 339.

to the formation of phenylmonobromlactic from phenylbibrompropionic acid, I undertook a study of these substances, and, although the work is not as yet completed, I have thought best to publish the few results so far obtained.

The two phenyltribrompropionic acids were obtained by Glaser by the action of bromine on the α- and β-monobromcinnamic acids, these two acids being formed by the action of alcoholic potash on phenylbibrompropionic acid.[1] In repeating this work I could not obtain a satisfactory yield of the monobromcinnamic acids; if, however, the ethyl ether, which is formed by the action of bromine on the ethyl ether of cinnamic acid,[2] is taken, the amount obtained averages nearly ninety per cent. of the theoretical.

The separation of the two monobrom-acids was effected by Glaser, by taking advantage of the differences in the solubility of their ammonium salts.[3] This seems to me unnecessary, as the α-acid itself is much less soluble in boiling water than the β-acid. Bromine, I found, would not act on the α-acid in a solution of bisulphide of carbon, and the tribrom-product was obtained by the action of bromine on the dry acid.[4] The substance formed is easily purified by recrystallization from bisulphide of carbon. It melts at 132° with slight decomposition.

Eight grams of this acid were placed in a flask with one hundred cubic centimeters of boiling water, and steam passed through the liquid; an oil was carried over, and the clear liquid on cooling deposited a crystalline substance, which had all the properties of α-monobromcinnamic acid, melting at 132.6°, soluble in boiling water, from which it crystallized on cooling.

A bromine determination gave the following results:

$$C_6H_5.CH=CBr.COOH.$$

Taken.	Found.	Calculated.
0.2300 gram	0.2216 gram AgBr.	
	35.37 per cent. Br.	35.25 per cent. Br.

The oil that was carried over by the steam was separated from the water by filtration, and after thorough washing to remove all the hydrobromic acid, was dried over sulphuric acid. Two determinations gave the following amounts of bromine:

Taken.	Found.		
0.2332 gram	0.3370 gram	AgBr = 61.48	per cent. Br.
0.2220 "	0.3213 "	AgBr 61.52	" Br.

[1] Ibid. **143**, 332.
[2] Berichte der deutschen chemischen Gesellschaft, **11**, 1219.
[3] Annalen der Chemie, **143**, 332.
[4] Ibid. **143**, 335.

This oil is evidently a bibromstyrene, the percentage of bromine required for that substance being 61.30. It is of a light yellow color, with an odor resembling bromstyrene. On being heated, hydrobromic acid is given off, and at a temperature of about 253° an oil begins to distill over. This oil was evidently a mixture, for on analysis it gave 59.35 per cent. bromine.

The decomposition of α-phenyltribrompropionic acid by water consists therefore in the splitting off both of bromine and hydrobromic acid, with the formation of α-monobromcinnamic acid and a bibromstyrene. The action of water on the β-tribrom-acid is without doubt analogous. This, together with a further study of the two tribrom-acids, and of the new bibromstyrene, I have already undertaken.

ON THE PROPYL DERIVATIVES AND DECOMPOSITION PRODUCTS OF ETHYL ACETOACETATE.

By Beverly S. Burton.

(Continued from Vol. 3, p. 395.)

Action of Phosphorus Pentachloride upon Diethyl Acetoacetate.

The action of phosphorus pentachloride upon ethyl acetoacetate was first studied by Geuther and Froehlich,[1] who obtained two isomeric chlorcrotonic acids. In all probability, the first phase of the reaction is the formation of the chloride of betadichlorbutyric acid, thus:

$$\begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CH_2 \\ | \\ CO.OC_2H_5 \end{array} + 2PCl_5 = 2POCl_3 + C_2H_5Cl + \begin{array}{l} CH_3 \\ | \\ CCl_2 \\ | \\ CH_2 \\ | \\ COCl \end{array}$$

This then loses hydrochloric acid, the hydrogen being taken, partly from the alpha-position and partly from the end methyl

[1] Zeitschrift für Chemie, 1869, 270.

group, and there are formed, simultaneously, the chlorides of the two isomeric chlorcrotonic acids:

$$a\begin{matrix}CH_3\\|\\CCl\\||\\CH_2\\|\\COCl\end{matrix} = a\,HCl + b\begin{matrix}CH_3\\|\\CCl\\||\\CH\\|\\COCl\end{matrix} + (a-b)\begin{matrix}CH_2\\||\\CCl\\|\\CH_2\\|\\COCl\end{matrix}$$

The liquid product gives the corresponding acids when treated with water, and these can be readily separated from each other by taking advantage of differences in their volatility and solubility. The chlorine atom in the two acids thus obtained can be readily replaced by hydrogen when treated with sodium amalgam.

Rücker[1] attempted later, by the action of phosphorus pentachloride upon methyl ethylacetoacetate, to obtain the corresponding isomeric methylcrotonic acids. There was, however, only a single methylchlorcrotonic acid obtained, which by the action of sodium amalgam could not be converted into methylcrotonic acid. It is then shown by these experiments of Rücker that there is a very marked and decided difference in the action of phosphorus pentachloride upon ethyl acetoacetate, and upon its methyl substitution product.

In view of these differences it was of special interest to further study the action of phosphorus chloride upon the dialkyl derivative of ethyl acetoacetate. It was to be expected that by the action of phosphorus chloride upon diethyl ethylacetoacetate the chloride of chlordiethylisocrotonic acid would be formed, thus:

$$\begin{matrix}CH_3\\|\\CO\\|\\C(C_2H_5)_2\\|\\CO.OC_2H_5\end{matrix} + 2PCl_5 = 2POCl_3 + HCl + C_2H_5Cl + \begin{matrix}CH_2\\||\\CCl\\|\\C(C_2H_5)_2\\|\\COCl\end{matrix}$$

The reaction does not, however, take place as here expressed, but the molecule is split up, as the following investigation shows.

The diethyl ethylacetoacetate was prepared according to the modified process of Conrad and Limpach, and that portion boil-

[1] Annalen der Chemie, **201**, 34.

ing between 210° and 215° was employed. In a flask connected with an inverted condenser were brought 65 grams (2½ mol.) of phosphorus chloride, and 20 grams of the ether were gradually added. Before heating, the action was very slight, but by gentle warming on the water-bath a very regular evolution of gas took place, which became violent when the temperature was increased to the boiling of water. The heating was continued for two days. When the reaction was complete, the product was poured into cold water; a heavy liquid separated and sank to the bottom. This was washed and dried over sulphuric acid. A portion was subjected to distillation. At 150° decomposition ensued, the liquid becoming dark and evolving acid fumes, but as the distillation in a current of steam could be effected, this method was employed. The product was separated from water and dried as before. This product is a colorless liquid, which by keeping turns slightly yellow and becomes acid. Concentrated solutions of alkaline carbonate and hydrate, even on boiling, had no noticeable effect upon it, clearly showing that the expected acid was not formed.

In the course of the experiments to be described later, it was found necessary to prepare a second portion of this product, which was carried out with every possible precaution and care. Repeatedly fractionated diethyl ethylacetoacetate, boiling between 210° and 212°, a combustion of which gave results agreeing closely with the theory, was treated as before with phosphorus pentachloride. The product was treated with sodium hydrate, thoroughly washed with water, dried over sulphuric acid, and then kept in contact with ignited potassium carbonate, the portions filtered off and employed for analysis were perfectly neutral to test-paper.

Under Nos. I. and II. are the results from the combustion of the product obtained by the first preparation.

Under III., IV., V., VI., VII., those from the second.

The results of the analyses in which lead chromate and a silver spiral were laid before the copper oxide are the following:

I.	0.2062	gram	substance	yielded	0.1333	gram	H_2O	and	0.3906	gram CO_2
II.	0.2054	"	"	"	0.1350	"	H_2O	"	0.3885	" CO_2
III.	0.2694	"	"	"	0.1804	"	H_2O	"	0.5113	" CO_2
IV.	0.2460	"	"	"	0.1648	"	H_2O	"	0.4675	" CO_2

Chlorine Determinations.

V. 0.4693 gram substance yielded 0.4125 gram AgCl
VI. 0.4518 " " " 0.3954 " AgCl
VII. 0.4571 " " " 0.3983 " AgCl

From the above is calculated the formula $C_7H_{11}ClO_2$.

	Calculated.	I.	II.	III.	IV.	V.	VI.	VII.
C_7	51.69	51.71	51.58	51.76	51.79	..	..	..
H_{11}	6.77	7.19	7.30	7.44	7.44	..	..	..
Cl	21.85	..	..	..	..	21.74	21.65	21.56
O_2	19.69	..	..	..	..	..	..	..
	100.00							

The chlorine was determined according to Carius's method. In order to effect a complete decomposition, it was found necessary to employ fuming nitric acid, and to maintain a temperature of 160° for several hours.

The anticipated dichlor substitution-product is not formed in the normal manner as expressed in the equation,

$$\begin{array}{l} CH_3 \\ | \\ CO \\ | \\ C(C_2H_5)_2 \\ | \\ CO.OC_2H_5 \end{array} + 2PCl_5 = \begin{array}{l} CH_3 \\ | \\ CCl_2 \\ | \\ C(C_2H_5)_2 \\ | \\ COCl \end{array} + 2POCl_3 + C_2H_5Cl,$$

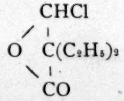
but decomposition ensues, one product of which is an oil containing chlorine. At the same time a gas is evolved, in all probability methyl chloride.

In order to study more closely the nature of this reaction, and to determine, if possible, the nature of the gaseous product, the above described process was repeated with the following modification: 67.2 grams (2 molecules) of phosphorus pentachloride were introduced into a flask connected with an inverted condenser, and the apparatus filled with carbon dioxide. There were now gradually added 30 grams of ether by means of a dropping funnel, and the evolved gases collected in a mercury gasometer, which contained a layer of strong caustic potash. In the course of several hours 200 cc. of gas were collected, this was dried by passing over calcium chloride, then conducted through two U-tubes, the first standing in a freezing mixture of ice and salt, the second in one of ice and crystallized calcium chloride which showed a temperature

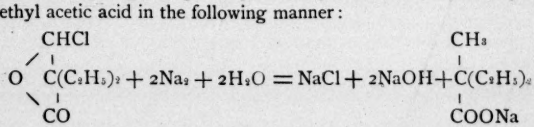
of −37°. As soon as the gas was driven out of the gasometer, the two tubes still in the freezing mixture were sealed by means of a blowpipe. In both were condensed a small quantity of liquid; that in the second tube disappeared when removed from the freezing mixture, but reappeared when again immersed. On opening the tube the gas, which violently escaped, burned with a green coloration of the flame, from which it may be concluded, with considerable probability, that this was methyl chloride. The first tube did not show these characteristics in so marked a manner, and was, apparently, ethyl chloride formed as indicated in the above equation. The splitting off of the methyl group is of special interest, as it is the first time that this phase of the decomposition of the ethyl acetoacetate molecule has been observed.

Action of Sodium Amalgam upon the Oily Product $C_7H_{11}ClO_2$.

It is difficult as yet to make any definite statement as to the constitution of the remarkable oily product corresponding to the empirical formula $C_7H_{11}ClO_2$. It possesses no acid properties, since it is not changed by caustic alkalies. It is rather to be regarded as a body with marked lactone characteristics, and possessed of great stability toward alkaline hydrates. That one of the oxygen atoms is present as carbonyl (CO) appears probable, and that the position of the two ethyl groups has not been changed, the chlorine atom being, without doubt, united with the ketone carbon atom of the diethyl acetoacetate. Assuming then the lactone character of the body, its constitution could be expressed by the formula.



It was now considered interesting to effect if possible the replacement of the chlorine atom by hydrogen by means of sodium amalgam, the further action of the sodium hydrate formed in the reaction giving rise, possibly, to a crystallizable salt of methyl-diethyl acetic acid in the following manner:



The product was mixed with alcohol, and water added until quite turbid. Then four per cent. sodium amalgam was introduced. The reaction took place slowly, and the volume of the oil decreased until it entirely disappeared in the resulting alkaline liquid. This was then neutralized with sulphuric acid, and repeatedly extracted with ether, separated, and the ether distilled off. The residue was again treated with sodium amalgam, neutralized, and extracted with ether as before, until all the oil was thoroughly decomposed. The neutralized solutions were then evaporated to dryness, and repeatedly extracted and purified with absolute alcohol.

The filtered alcoholic solutions left, on evaporation, an extremely deliquescent sodium salt, which, however, still contained a very little chlorine. A small portion acidified with sulphuric acid deposited oily drops, which possessed the characteristic odor of the higher fatty acids.

An attempt was made to remove the chlorine present by partial precipitation with silver nitrate, which was continued until the formed precipitate dissolved clear in nitric acid, then all was precipitated with silver nitrate. The separated organic silver salt formed a white powder, not readily affected by light, which could be dried without decomposition. The analysis yielded the following results:

I. 0.2368 gram silver salt yielded 0.2712 gram CO_2, 0.0975 gram H_2O, and 0.1156 gram residue.

II. 0.2098 gram silver salt yielded 0.2400 gram CO_2, 0.0861 gram H_2O, and 0.1027 gram residue.

The percentage composition calculated from the above is:

	I.	II.
C	31.24	31.21
H	4.58	4.56
Residue	48.82	48.95

An examination of the residue showed that 0.1156 gram of the same contained 0.0300 gram of silver chloride.

By protracted boiling of the silver salt with a large amount of water and allowing to cool, various portions of crystallized salt were obtained. Two different portions yielded the following results:

I. 0.1943 gram silver salt yielded 0.2352 gram CO_2, 0.0841 gram H_2O, and 0.0936 gram residue. 0.0616 gram residue contained 0.0320 gram silver chloride=4.37 per cent. Cl.

II. 0.1912 gram silver salt yielded 0.2233 gram CO_2, 0.0799 gram H_2O, and 0.0919 gram residue. 0.0583 gram residue contained 0.0336 gram silver chloride=4.35 per cent. Cl.

Expressed in percentages:

	I.	II.
C	33.01	31.85
H	4.81	4.64
Residue	48.17	48.07

The composition had thus not materially changed, and no formula could be calculated. A determination of the chlorine was then made by Carius's method.

0.3942 gram of the silver salt gave, by complete oxidation with fuming nitric acid in a sealed tube, 0.0670 gram silver chloride, corresponding to 4.20 per cent. chlorine. This chlorine residue is due, undoubtedly, to the presence of an organic acid containing chlorine.

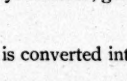
An experiment showed that the acid mixture separated by a mineral acid could be distilled without decomposition, and this method was now resorted to for its purification. The sodium salt was decomposed with very dilute sulphuric acid, the oily layer separated, and the aqueous solution extracted with ether. The acid so obtained was then subjected to fractional distillation. The boiling point rose very rapidly to 185°; by far the greater portion distilling over at 190°–192°, leaving a residue which on heating evolved fumes of hydrochloric acid. After repeated distillation the fraction 190°—192° showed on ignition with sodium only traces of chlorine. A combustion was then made yielding the following results:

I. 0.1832 gram of acid gave 0.4127 gram CO_2, and 0.1759 gram H_2O.

II. 0.1922 gram of acid gave 0.4355 gram CO_2, and 0.1796 gram H_2O.

From this is calculated the formula of diethylacetic acid, with which this acid fully agrees in boiling point and all other properties.

	Calculated.	Found. I.	II.
C_6	62.07	61.44	61.80
H_{12}	10.34	10.67	10.38
O_2	27.59	...	...
	100.00	...	...

By far the larger portion of the oil $C_7H_{11}ClO_2$ is then, by treatment with sodium amalgam, converted into diethylacetic acid. What is formed here at the same time as a by-product in the reaction I have not been able as yet definitely to determine. The fact, however, of the splitting off of a carbon atom is established, completing and confirming the observations previously made as to the slight binding power or affinity of the carbon atom, combined with the two alkyl groups, and the carbon atom of the ketone group in the diethyl acetoacetates. By saponification with alkalies, diethyl acetoacetate splits up into diethylacetic acid and acetic acid. By heating diethyl betaoxybutyric acid splits up into diethylacetic acid and aldehyde, as does also dipropyl acetoacetate by the mere attempt to convert it into the corresponding oxyacid, and so, finally, phosphorus pentachloride splits up the molecule of diethyl acetoacetate, though not at the same point, the first phase in the reaction being the removal of the methyl group which escapes as methyl chloride, giving rise to a compound which, in contact with water, is converted into the body  , of the nature of an anhydride such as lactone; and this by further treatment with sodium amalgam suffers the normal decomposition of the dialkyl acetoacetate already mentioned, giving rise to diethyl acetic acid.

I desire to express here my thanks to Professor Wislicenus, in whose laboratory these investigations were carried out, for his uniform kindness and many valuable suggestions.

Contributions from the Sheffield Laboratory of Yale College.

XI.—ON UREA FROM AMMONIA AND CARBON DIOXIDE.

By W. G. Mixter.

The well-known formation of urea when ammonium carbamate is heated in sealed tubes to 140°C. suggested the possibility of making urea by passing ammonia and carbon dioxide through a warm tube. It was found, however, that the two gases do not react on each other at temperatures somewhat below a visible red, but that at a red heat products are formed which yield urea beautifully crystallized in the cooler parts of the tube, where the heat nevertheless is sufficient to prevent the condensation of ammonium carbamate and carbonates. The urea forms very slowly, and the yield is apparently not increased by heating a greater length of tube, or by passing the gases over charcoal or platinized asbestos. The greater part of the ammonia and carbon dioxide passes unchanged, and more water is formed than corresponds to the urea produced. The substance used for analysis was made as follows: Dry ammonia and carbon dioxide were passed separately into the hot part of a combustion tube, which was heated to redness in a combustion furnace by four or five burners. A second portion of the tube eight or nine inches from the first hot part was also heated. To facilitate condensation, the tube, which was about two centimeters wide, was enlarged to bulbs of four or five centimeters in the parts anterior to the heated places. The bulbs were protected from the intense heat by screens, and were usually hot enough to prevent the deposition of ammonium salts. If these condensed with the urea, they were driven off by careful heating. The urea formed at the rate of a decigram to decigram and a half an hour. A slight opaque white sublimate formed between the urea and the hot part of the tube. The urea was dissolved in absolute alcohol, the solution was evaporated and the residue was dried at 100°C., and finally in a vacuum over oil of vitriol. It melted at 131°C.[1]

[1] Lubavin, Berichte der deutschen chem. Gesell. **3**, 303, found the melting point of urea from potassium cyanate to be 132°C.

The nitrogen was determined by a combustion with soda-lime and titration.

	Urea.	Found.	
C	20.	20.50	20.29
H	6.66	6.86	6.79
N	46.67	46.14	
O	26.67		

The excess of carbon and the deficiency of nitrogen found is doubtless due to the loss of some ammonia during the long exposure to heat in making. A titration with mercuric nitrate solution gave 99.02 per cent. of urea. The identity of the substance with urea was further confirmed by the following properties: It gave off ammonia when heated, and the residue gave the biuret reaction with copper sulphate and caustic potash. It did not react for biuret or cyanuric acid before heating. The nitrate separated on adding nitric acid to the aqueous solution in apparently the characteristic form of urea nitrate.

It is evident that urea is not the direct product of the reaction between carbon dioxide and ammonia, as it is decomposed at the temperature used in the experiment.

The formation of urea in the way described is undoubtedly preceded by the formation of other bodies, and probably by the production of cyanic acid, thus:

$$CO_2 + NH_3 = HCNO + H_2O.$$

If cyanic acid is formed it would unite with ammonia in the cooler part of the tube to form urea, as was proved by passing cyanic acid, prepared from cyanuric acid, and ammonia through a red-hot tube. The reaction here suggested as probable is analogous to that which, according to Kuhlmann, occurs when ammonia and carbon monoxide are passed over heated platinum sponge in a tube,[1] the final product of which may be represented thus:

$$CO + 2NH_3 = NH_4CN + H_2O.$$

But since ammonium cyanide cannot exist at a high temperature, hydrocyanic acid is doubtless first formed and combines with ammonia in a cooler part of the apparatus,

$$(NH_3 + CO = HCN + H_2O \text{ and } HCN + NH_3 = NH_4CN).$$

[1] Graham-Otto **1**, 1127.

Further evidence that the production of cyanic acid precedes the formation of urea was found in the fact that alkali cyanates are formed when ammonia and carbon dioxide pass over hot alkali carbonates.

Herroun[1] obtained urea by passing air, ammonia and benzene vapor over a hot coil of platinum. In view of the results of the above described experiment, it seems reasonable to suppose that the urea which Herroun obtained resulted also from the action of carbon dioxide on ammonia, since benzene with an excess of air would produce carbon dioxide.

On Cyanates from Ammonia and Carbon Dioxide.

If the assumption is correct that the formation of urea in the foregoing experiment is preceded by the formation of cyanic acid, the production of cyanates might be expected if some substance capable of combining with that body were present. The result of the following experiments shows that cyanates are actually formed under such conditions. A preliminary trial was made by passing cyanic acid from cyanuric acid over red-hot magnesia, lime and sodium carbonate. The first two did not take up cyanic acid, while the latter was partially converted into sodium cyanate. Dry carbon dioxide and pure dry ammonia were passed through a combustion tube containing sodium carbonate heated to redness, but not hot enough to fuse the pure carbonate. The mass in the tube began to soften at the end where the gases first came in contact with it. As soon as one part was fused the heat was lowered somewhat to prevent danger from overheating and partial decomposition of the cyanate formed. In an hour the experiment was ended, and the flow of the ammonia was then stopped, and the current of the carbon dioxide was continued a few minutes to expel the ammonia. The saline mass gave off ammonia very slowly on boiling with water, but after saturating with hydrochloric acid and adding an excess of caustic potash, ammonia was freely evolved. 3.4 per cent. of nitrogen[2] were found in a portion where the gases first came in contact with the sodium carbonate, and 1.1

[1] J. Chem. Soc. Oct. 1881, 471.

[2] The method used in estimating nitrogen is based on the formation of ammonium salts when cyanates are treated with an acid. Two test determinations of the nitrogen in pure potassium cyanate were made by dissolving the salt in dilute hydrochloric acid, then adding potash and distilling into standard acid and titrating; 16.06 and 16.07 per cent. of nitrogen were found; theory requires 17.02 per cent. Whether the loss was due entirely to the setting free of some cyanic acid, by the action of the acid on the cyanate, was not determined. All the nitrogen estimations were made by this method.

per cent. in a part near the open end of the combustion tube. Potassium carbonate behaves like sodium carbonate and yields a product more fusible than potassium carbonate. In one experiment a portion from near the posterior end of the tube in which the carbonate was heated yielded 4.3 per cent. of nitrogen, corresponding to 25 per cent. of potassium cyanate. This product from the potassium carbonate gave the odor of cyanic acid when dissolved in dilute hydrochloric acid. Another part of the same product was dissolved in water, ammonium sulphate was added and the whole was evaporated, the residue was exhausted with alcohol, and from the alcoholic solution urea was obtained.

It must be admitted that the production of cyanates by this method does not positively prove the previous formation of cyanic acid, since some cyanate is formed by the reaction of ammonia alone on sodium carbonate. In one experiment dry ammonia was passed over sodium carbonate which was gradually heated to fusion, and 1.2 per cent. of nitrogen was found in the product. A similar experiment in which potassium carbonate was used yielded 1.1 per cent. of nitrogen. These amounts of nitrogen, which were the highest obtained in several such experiments, show that from one-quarter to one-third as much cyanate was formed as when carbon dioxide was used.

It should be mentioned that, in making cyanates from alkali carbonates, ammonia and carbon dioxide, no cyanides were formed when pure ammonia[1] was used, but that when ammonia gas from a good quality of commercial ammonia water was used, the solution of the saline mass reacted distinctly for cyanides with ferroso-ferric sulphate and an acid.

When soda-lime is exposed to the combined action of carbon dioxide and ammonia, only that portion next the posterior end of the heated tube yields ammonia, and only traces of it. Dr. E. H. Jenkins informed the writer that he obtained no ammonia on boiling the soda-lime after making a combustion of dried blood.

[1] The pure ammonia was prepared from sal ammoniac which was freed by Stas's method from compound ammonias by boiling a saturated solution with nitric acid. The ammonia was liberated by lime and dried by caustic potash.

ACONITIC ACID IN THE SCALE FROM SORGHUM SUGAR PANS.

By Henry B. Parsons.

Clear, defecated sorghum juice, after treatment with milk of lime to faint alkalinity, slowly deposits, on further boiling, a light buff-colored scale, which adheres tenaciously to the evaporating pan, and, being a poor conductor, causes a considerable loss of available heat.

This scale is easily soluble, without effervescence, in hydrochloric acid, the resulting solution giving abundant evidence of lime and magnesia, but no tests for sulphate, glucose, or sucrose; hence the scale is neither calcium sulphate nor any compound of lime with sucrose, as was at first surmised.

A careful analysis of an air-dry sample resulted as follows:

Analysis of Scale from Sorghum-Sugar Pans.

Moisture, loss at 125° C.	7.48
Silica and clay, insoluble in HCl	1.57
Oxides of iron, aluminium, and manganese,	.57
Phosphoric anhydride (P_2O_5)	.19
Calcium oxide, (CaO)	22.87
Magnesium oxide, (MgO)	3.65
Alkalies,	traces
Organic matter, by difference,	63.67
	100.00

As lime was originally used in excess, the magnesia present was believed to be in the form of oxide, uncombined with the organic matter at least, though a portion may have been combined as phosphate. Rejecting accidental impurities and considering this scale as an impure lime salt, we have:

	Obtained.	In 100 Parts.
Water, H_2O,	7.48	7.95
Calcium oxide, CaO,	22.87	24.32
Organic,	63.67	67.73
	94.02	100.00

Upon dividing the figures in the second column by the molecular weights, respectively, of water, calcium oxide, and the calculated molecular weight of the organic matter, we obtain results which leave little room for doubt that this substance is a simple, definite salt of calcium: thus:

Water, H_2O,	$7.95 \div 18$	$= .4417 = 1$
Calcium oxide, CaO,	$24.32 \div 56$	$= .4343 = 1$
Organic,	$67.73 \div 155.3$	$= .4361 = 1$

A small portion of what proved to be the organic acid was separated in nearly pure condition, by boiling the finely pulverized scale with an amount of dilute sulphuric acid not sufficient to combine with all the lime and magnesia present.

The clear, golden-yellow filtrate had a strong acid reaction not due to sulphuric acid, and contained considerable magnesium sulphate, a little calcium sulphate, and a small amount of manganese as soluble salt. Upon treating this solution with twice its volume of absolute alcohol the calcium and magnesium sulphates were precipated. The filtrate, evaporated to a small bulk, was treated with excess of absolute alcohol, whereby a magnesium salt of the organic acid was precipitated.

This salt (A) was well washed with absolute alcohol, then with ether, dried and pulverized; it was nearly white. Upon gentle ignition a pink residue remained, which became dark brown upon further heating. As this salt (A) was perfectly soluble in water, and as inorganic acids were proved to be absent, it appears that manganous oxide must have partially replaced the magnesium oxide in this salt. The following is the analysis:

Composition of Magnesium Salt. (A).

	Air Dry.	Dried at 125° C.
Water, H_2O,	9.97	...
Manganous oxide, MnO,	.98	1.09
Calcium oxide, CaO,	5.20	5.78
Magnesium oxide, MgO,	14.05	15.60
Organic, by difference,	69.80	77.53
	100.00	100.00

Calculating the manganous and calcium oxides to their magnesium oxide equivalents, we have for the dry salt:

Magnesium oxide, MgO,	$20.35 \div 40.0$	$= .5088 = 1$
Organic,	$79.65 \div 156.6$	$= .5086 = 1$

An aqueous solution of this salt gave the following reactions:

Silver Nitrate: A scanty white precipitate, dissolved and blackened by boiling.

Lead Acetate: A bulky white precipitate.

Mercuric Chloride: A moderate amount of yellowish-white precipitate.

Mercuric Nitrate: A bulky white precipitate.

Copper Sulphate: A bulky white precipitate.

Ferric Chloride: Concentrated solution, a bulky gelatinous, yellowish-red precipitate.

Barium Chloride: No precipitate.

These reactions led to the belief that the acid must be *aconitic*, and further study and analytical results confirm this opinion.

The filtrate from salt (A) was concentrated until free from alcohol, and after cooling, treated with excess of stronger ether, whereby a yellowish, stringy, hygroscopic mass was precipitated; this proved to be a mixture of salt (A) with free organic acid. It was freely soluble in water, partially in alcohol. It was not further examined.

The ethereal filtrate from this treatment had a lemon-yellow color, a strong acid reaction, and when heated, gave off acid vapors, took fire readily, and left an unweighable ash. A second solution in ether and filtration furnished the ash-free acid, which slowly crystallized in imperfect warty masses. From this acid the zinc, lead, and silver salts were prepared as follows:

1. *Zinc Salt.*—A dilute aqueous solution of the acid was heated for several hours on the water-bath with excess of pure zinc oxide. The filtrate was evaporated and dried at 110° C. to a constant weight. Continuous ignition, with use of nitric acid, left a residue of zinc oxide equal to 34.15 per cent. of the dry salt.

2. *Lead Salt.*—A slightly alkaline (ammoniacal) solution of the acid was made faintly acid with acetic acid and precipitated by normal lead acetate. The white precipitate was washed with water in a Gooch crucible, dried *in vacuo*, and to a constant weight at 100° C., and carefully ignited; 69.18 per cent. of lead oxide was thus obtained.

3. *Silver Salt.*—A cold, neutral ammonium salt of the acid was precipitated by the solution of silver nitrate, the white precipitate well washed, dried at 110° C., and ignited. This salt was slightly blackened and decomposed about the edges before ignition; 64.42 per cent. of silver was found.

Owing to lack of material no further determinations were made, yet it is believed that the following results taken in connection with the exact correspondence in qualitative reactions, will justify the assertion that this sorghum-sugar scale is a two-thirds metallic calcic aconitate containing one molecule of combined water ($CaHC_6H_3O_6.H_2O$).

	Formula.	Sought.	Found.	Theory.
Calcium salt,	$CaHC_6H_3O_6.H_2O$,	CaO,	24.32	24.35
		H_2O,	7.95	7.82
Magnesium salt,	$MgHC_6H_3O_6$,	MgO,	20.35	20.41
Zinc salt,	$ZnHC_6H_3O_6$,	ZnO,	34.15	34.22
Lead salt,	$Pb_3(C_6H_3O_6)_2$,	PbO,	69.18	69.42
Silver salt,	$Ag_3C_6H_3O_6$,	Ag,	64.42	65.38

The presence of aconitic acid in meladoes from the West Indies was proved by A. Behr;[1] the presence of the same acid in the juice of sorghum, a plant somewhat closely related to sugar cane, is interesting in that it is another instance of the many similarities in chemical composition which have been noted of late years, in plants of the same or closely allied families and orders.

I am indebted to Mr. Clifford Richardson, of the Department of Agriculture, Washington, D. C., for the completion of work upon the lead, silver, and zinc salts.

New York, Jan. 1882.

APPARATUS FOR THE ABSOLUTE DETERMINATION OF NITROGEN.

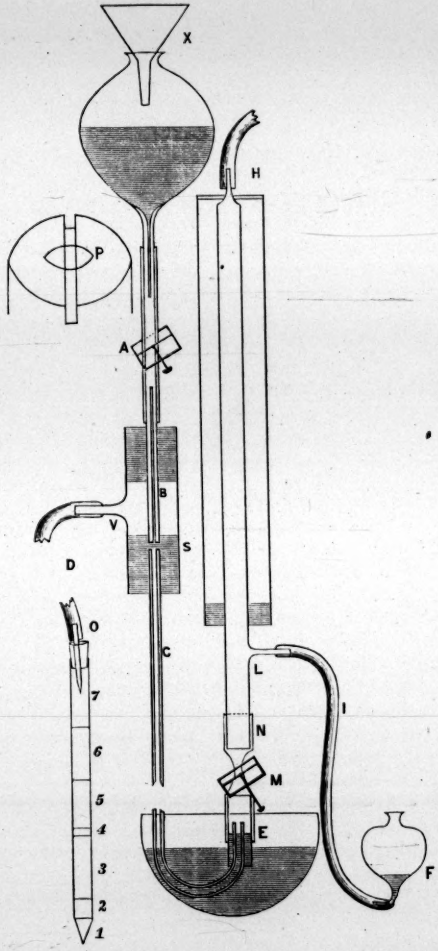
By Thomas S. Gladding.

The great value of the azotometer and mercury pump, devised by Professors S. W. Johnson and E. H. Jenkins,[1] and their rapidly extending use, will make any worthy improvement thereon welcome.

In the accompanying cut, improvement has been sought on four points.

1st. In a more rapid exhaustion of the combustion tube.

[1] Berichte der deutschen chemischen Gesellschaft, **10**, 351.


X
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2d. In a simpler and easier method of collecting the nitrogen gas.

3d. In the attainment of a constant suction on the combustion tube, thereby preventing blowing-out of the tube, so frequently a source of trouble to the analyst; and

4th. In the more thorough preliminary exhaustion of the combustion tube and the consequent greater accuracy of the analysis.

A few words only will be needed to explain the accompanying section of the apparatus. Upon the side of the glass tube S is blown a stout piece of glass tubing V. The pure (so called) rubber tubing D, with walls 4 mm. thick to prevent collapse from atmospheric pressure, serves to connect the pump with the combustion tube, and is securely bound to the tubes V and O (which are previously smeared with glycerine) by means of copper wire wound as tightly as possible. This tube D is clamped securely to the wooden frame of the apparatus just beyond the glass tube V, in order to remove the latter from all strain. The barometer tubing C, 7 mm. in diameter, is forced up to within 5 mm. of the top of the rubber cork S. The tube B is forced through the cork B into the cork S to within 1 mm. of the tube C. The bore of B is about one-half that of C and is held exactly over the latter. The flow of mercury is regulated by the clamp A. The rubber tube A is bound tightly to B, its walls are 2 mm. thick, and it is wrapped with one layer of kid or chamois skin to prevent wear by the action of the clamp A. The tube C is about 45 inches in length and curves up into the glass tube E. A stout glass finger-bowl is admirably adapted to serve as the vessel E. The tube E is connected with N by a large rubber tube tightly bound to both and closed at pleasure by the large screw clamp M. The cork S is shown in nearly top section at P. A slot about 3 mm. wide and 5 mm. deep is cut straight across the cork. In this way free access of the gas to be pumped off is given into the tube C, and at the same time the tube B is held exactly over the former.

The first point of improvement, viz. the more rapid exhaustion of the air in the combustion tube, is obtained by the peculiar construction of the pump. The tube B delivers exactly into C, and the bore of C being larger than that of B, there is no choking. The bore of C may be as large as 2 mm. With such a size a complete

[1] This Journal, 2, 27.

vacuum in the combustion tube is easily obtained in from four to five minutes.

The second point of improvement is understood from the figure. The curving of the tube C up into E for the distance of 1½ inches removes all danger of loss of nitrogen and all necessity of handling or moving about any part of the apparatus.

The third point is obtained by the method of collecting the gas. When M is open and the reservoir F is placed a few inches below the level of the mercury in the vessel E, the pressure upon the mercury in the tube E is diminished, the mercury rises slightly in the tube E, and the internal pressure upon the walls of the combustion tube is correspondingly diminished. Provided no stoppage takes place in the tube itself from too close packing or the use of too fine a filling, no tube can blow out if this device is used. This suction may be increased at pleasure by lowering the vessel F still more, but a gentle aspiration is usually sufficient and safer.

The fourth point, a more thorough exhaustion of the gas in the combustion tube, is effected as follows: About 0.6 gram of bicarbonate of soda is placed in the tail of the tube at 1. The use of chlorate of potash has been found unnecessary in all ordinary work, from duplicate analyses performed with and without it. Its use introduces, moreover, a possible escape of oxygen gas beyond the metallic copper and a consequent error in the analysis. The space 2, about two inches in length, is filled with ignited asbestus. This is followed by the substance to be analyzed at 3, mixed with copper oxide. This latter is about as fine as sea-sand, and is freed from dust or pulverized copper oxide by means of a fine sieve. It is strongly ignited and mixed with the substance while still warm. At space 4 is another 0.6 gram of bicarbonate of soda. This is followed by a layer of copper shot at 5, and this again by a layer of coarsely granulated copper oxide. The analysis is begun by drawing the potash solution nearly to the top of the azotometer, then turning up lamps under 6 and at the same time starting the pump. When a perfect vacuum has been obtained and the copper oxide 6 is red hot, the lamp just beyond 1 is turned up, and a gentle heat just sufficient to drive off the CO_2 from it and not to heat space 3 is applied. When the tube is full of CO_2 this lamp is turned off and the tube again exhausted. By this process of washing out the tube, several tenths of a cc. of additional gas are obtained, and almost the last traces of air are removed. The object in using finely

granulated copper oxide free from the powder is to give full play to this washing. On running the heat back the bicarbonate at 4 gives off CO_2 and refills the tube before the combustion of the substance at 3 begins. At this stage, draw the potash solution again up to H.

To fill the azotometer with the potash solution, pinch the rubber tube I, and by the suction of the mouth applied at the rubber tube H draw the mercury up as far as the tube L. Holding it there, close the clamp M, raise the reservoir F and fill it with the potash, which rises of course in the azotometer LH.

While the apparatus is in this condition, the tube remaining filled with mercury from M to L, the azotometer may be lifted and removed from the pump for any repairs without mixing the mercury and potash solution. In this position also it may be washed out for a fresh filling. Lower the reservoir F and invert it into a beaker. Upon opening the cock H all the potash runs out, and the tube HL may be rinsed clean with dilute acid introduced at H. The potash in tube LH may be drawn up to the glass cock H, either by closing the clamp M and then raising F to the level of H. or by the suction of the mouth applied at the rubber tube H. When the apparatus is not in use, F should be on a level with E to prevent any possible aspiration of air into the azotometer tube from the tube C.

Two simple rules may be given to prevent the potash solution in N from ever escaping into the vessel E: Close clamp M (1) whenever F is to be raised above E; (2) whenever the glass cock H is to be opened.

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THE ESTIMATION OF UREA BY SODIUM HYPOBROMITE.

By J. R. Duggan.

Since Knop, in 1854, announced his method for the estimation of urea by the amount of nitrogen evolved on the addition of an alkaline hypobromite, there has been considerable discussion concerning its accuracy. The method requires so little time and skill in its application, that this question is the only one necessary to decide its precedence over all others. Although a few observers have obtained nearly perfect results in its use, it is generally admitted that only about 92 per cent. of the whole amount of nitrogen is liberated by the hypobromite; and this error is not very constant. For clinical purposes even this approximation is of value, but in physiological investigations greater accuracy is required.

Some time ago I began work on this method to find what conditions were necessary to give the best and most uniform results. After a large number of determinations of nitrogen evolved from a standard solution of urea, I found that the largest quantity was liberated by a solution containing the caustic soda and bromine in about the proportion recommended by Knop, but considerably more concentrated. A solution made up of 20 grams of caustic soda and 5 cc. of bromine, and anywhere from 50 to 100 cc. of water, gave fairly uniform results, and from five to ten per cent. more nitrogen than the more dilute solutions. In order to avoid as much as possible too rapid action and spurting, I prefer the solution made up with 100 cc. of water to the more concentrated. Even with this solution I was seldom able to obtain 92 per cent. of the known amount of nitrogen in a standard solution of urea.

In trying to find some method by which I could effect the complete decomposition of the urea and liberation of all the nitrogen, it occurred to me to mix the urea and the caustic soda solutions and then add the bromine. I hoped that by forming in this way

the hypobromite in the presence of the urea to accomplish my purpose.

The first experiment with this method gave better results than I had at any time obtained in the old way. I then began a series of experiments to find how much of the nitrogen was liberated by this modification of Knop's method. The following table gives the results of a few of these:

No.	Amount of Urea.	Bar.	Temp.	Vol. of Nitrogen.	Weight of N.	Weight of Urea.	Per Ct.
1.	3 cc. 3 per ct. urea solution,	767	21°	36.35	41.75	89.47	99.40
2.	" " " "	767	21	36.30	41.70	89.36	99.29
3.	" " " "	767	21.5	36.50	41.82	89.62	99.57
4.	2 cc. " " "	767	21	24.20	27.80	59.56	99.29
5.	" " " "	767	21.8	24.30	27.80	59.56	99.29
6.	" " " "	765	21.5	24.45	27.94	59.88	99.77
7.	5 cc. 2 per ct. urea solution,	765	20.8	40.30	46.21	99.02	99.02
8.	" " " "	765	21	40.40	46.28	99.17	99.17
9.	" " " "	765	20	40.50	46.62	99.91	99.91
10.	3 cc. " " "	765	20.9	24.33	27.88	59.74	99.59
11.	" " " "	765	21	24.38	27.93	59.85	99.75
12.	" " " "	765	21	24.26	27.73	59.43	99.04
13.	7 cc. 1 per ct. urea solution,	765	21.6	28.40	32.44	69.52	99.30
14.	" " " "	765	22	28.40	32.37	69.37	99.10
15.	" " " "	765	22	28.60	32.60	69.86	99.79

The form of apparatus used in these experiments is the same as that generally used with the old method. It consists of a small flask or bottle, a specimen tube, a burette, and a tall glass cylinder. The flask is closed with a rubber stopper having two perforations. Through one of these passes a tube which is connected by rubber tubing to the burette. Through the other passes a short tube which opens externally, but may be closed by a pinchcock and a bit of rubber tubing. The tall cylinder is filled with water, and the burette inverted in it. The requisite quantities of the caustic soda and the urea solutions are placed in the flask, and the specimen tube, into which the bromine has been placed, is set in this, inclined against the side of the flask so that it will not overturn. The stopper being inserted, the flask is immersed in a large vessel of water whose temperature is noted, and allowed to remain until its temperature is constant. The burette is elevated until the level of the water is exactly at zero, and the pinchcock then closed. By tilting the flask to one side, the bromine may now be allowed to run slowly out and mix with the caustic soda and urea solutions.

The evolution of nitrogen takes place rapidly, and in a few minutes the reaction is completed. The flask should be shaken until all the bromine has disappeared. It is then replaced in the large vessel of water to reduce it to its original temperature. The burette being elevated until the water is at the same level inside and out, the volume of gas is read off and corrected for temperature and barometric pressure. About forty minutes are required for each determination. The burette should be allowed to remain elevated out of the water sufficiently long before reading for the inclosed gas to acquire the temperature of the surrounding atmosphere. In order to prevent any elevation of temperature in the water surrounding the flask by the reaction, I found it convenient to cool the flask in another vessel containing water of about the same temperature, before replacing it.

The caustic soda solution is made by dissolving 20 grams of sodium hydrate in 100 cc. of water. With each 20 cc. of this there should be used 1 cc. of bromine. In the series of experiments already given I used in each from 20 to 30 cc. of the caustic soda solution, and from 1 to 1.5 cc. of bromine. The relative amounts of caustic soda and bromine should not vary, but it is not necessary to be very exact in the quantities used. When determining urea in very dilute solutions, or in very small quantities, it would be advisable to use proportionately small quantities of the reagents.

The most troublesome part of the experiment is the measuring out of the bromine; but if a few drops of water be placed in the specimen tube it will float on top, and prevent, to a great extent, the escape of the bromine vapor.

For calculating results I have found the method given by Franklyn in his "Water Analysis" to be by far the best. The weight of nitrogen multiplied by 2.143 gives the amount of urea.

I expect in the future to apply this method to the determination of nitrogen in other organic compounds, as I think it probable that it will give as accurate results as with urea.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY, *March*, 1882.

ON THE TRANSFORMATION OF OZONE INTO OXYGEN BY HEAT.

By Ira Remsen.

It is known that when ozone is heated to about 200° it is converted into oxygen. Accepting the prevalent view concerning the nature of ozone, but two conceptions regarding this transformation appear at all probable. If the molecule of ozone contains three atoms, and that of oxygen two, then the transformation of the former into the latter by heat consists, first, in the partial decomposition of the molecule, either into a molecule and an atom of oxygen, or into free atoms only, and, second, in the recombination of the free atoms to form molecules of ordinary oxygen. Though the interval of time between the decomposition of the ozone and the formation of the oxygen molecules may be infinitesimal, there must apparently be this interval, and then the oxygen should be in its most active state with the powers that characterize nascent oxygen. But ozone itself, as is well known, is a strong oxidizing agent, so that to distinguish between nascent oxygen and ozone appears at first to be a very difficult problem. A recent interesting communication[1] by E. Baumann shows how this may be done, and I am hence led to describe an experiment which was performed in this laboratory some time since by Mr. P. H. Broun, the results of which are especially noteworthy, as they seem to throw some light on the processes involved in the transformation of ozone into oxygen under the influence of heat.

Southworth and I have shown[2] that ozone does not oxidize carbon monoxide. Baumann confirms this, and further proves that nascent oxygen, obtained by the action of palladium-hydrogen on oxygen, does transform the monoxide into the dioxide. This difference in the conduct of the two substances furnishes a means of distinguishing between them. If in any gaseous mixture there is ozone and no nascent oxygen, carbon monoxide will not be

[1] Zeitschrift für physiologische Chemie, **5**, 244.

[2] American Journal of Science, **11**, 136; and Berichte der deutschen chemischen Gesellschaft, **8**, 1415.

oxidized by it. On the other hand, if nascent oxygen be present, carbon monoxide will be converted into carbon dioxide.

Having proved beyond a doubt that carbon monoxide is not oxidized by ozone at the ordinary temperature, it remained to determine at what temperature the oxidation is effected. It seemed probable that this temperature would be below that at which ozone is transformed into oxygen, or, if not, then at least at the transformation temperature. Mr. Broun's experiments above referred to, led to what appears to me to be an astonishing result, viz., that carbon monoxide is not oxidized by ozone even at the temperature at which the ozone is transformed into oxygen. For various reasons the experiments were left in a somewhat unsatisfactory shape, and recently, at my suggestion, they have been repeated by Mr. E. H. Keiser. Every precaution was taken to avoid error, and the result reached fully confirms the conclusion just stated. Before discussing this result in its relations to the nature of the molecule of ozone, I will describe in detail the experiments which led to it.

A gasometer was filled with pure carbon monoxide, made from potassium ferrocyanide and sulphuric acid, and purified by passage through four wash-bottles containing caustic soda solution. Another gasometer was filled with pure oxygen. In the first experiments the oxygen was ozonized by means of a Siemens tube connected with an efficient induction coil. It was afterwards found, however, that much stronger ozone could be obtained by the use of Wright's tube connected with a Holtz electrical machine. It is hence only necessary to describe one of the experiments made with the latter form of apparatus. A slow current of oxygen from the gasometer was passed through three wash-bottles containing caustic soda solution, and then through the ozonizer. The ozone was tested and found to be unusually strong. The greatest care had to be taken to avoid the exposure of rubber to its action, as it required but momentary contact to effect the perforation of the rubber. The carbon monoxide was passed through wash-bottles containing caustic soda solution and finally through baryta water. The two gases were then brought together in a U-tube placed in an air-bath. After leaving the U-tube the gases passed through perfectly clear lime-water. The mixture in the U-tube was heated gradually to about 300°. Under these conditions the current of the gases was continued for an hour, and no precipitate was formed in

the lime-water. Separate experiments were made for the purpose of determining how readily the ozone was destroyed, and it was found that, even when the thermometer in the U-tube indicated a temperature considerably below that stated as the decomposition temperature of ozone, and when highly ozonized oxygen was certainly passing into the U-tube, no ozone passed out, whether carbon monoxide was present or not in the tube at the same time. The experiment as above described was repeated several times, but always with the same result. One modification of the experiment should also be mentioned in this connection. In order to get as good ozone as possible, the ozonizer was filled with oxygen, and the current of gas then stopped. The oxygen was left in the tube for a minute or two, and then passed slowly into the heated U-tube containing the carbon monoxide. This interrupted current of oxygen was continued for about an hour, but no oxidation of carbon monoxide to the dioxide could be detected.

It is difficult to see how the fact thus established can be explained, if we accept the prevailing ideas concerning the nature of ozone, and its transformation into oxygen by heat That carbon monoxide can unite with oxygen when the latter is in proper condition is established. We cannot conceive of a more favorable condition for this union than that presented by free atoms of oxygen. When ozone passes into the form of oxygen under the influence of heat, are there not formed free atoms of oxygen? If not, then how does this change take place? If the molecule of ozone consists of an odd number of oxygen atoms, free atoms must apparently be formed during the change. We may, to be sure, conceive of the change as possibly taking place in this way. Two ozone molecules, after being partly broken up, may unite, forming a more complex molecule of six atoms, and this may then break up in pairs of atoms or into oxygen molecules. Even this would involve, as far as we can form any conception of such a process, a temporary increase in the activity of the oxygen. Speculation in this direction can, however, have but very little value at present.

Another thought suggests itself. Hoppe-Seyler and Baumann hold that the energetic oxidizing action of palladium-hydrogen and oxygen is due to the formation of nascent oxygen. While this explanation appears probable, it certainly lacks adequate proof. The action may be more complicated than this explanation

would make it appear. On the other hand, Moritz Traube's statement[1] that the action is due to the formation of hydrogen dioxide would appear to be disproved by the fact that, while carbon monoxide is oxidized by palladium-hydrogen in the presence of oxygen, it is not oxidized by hydrogen dioxide, as was shown by me some time since.[2] The experiments upon which my statement on this point was originally based have been recently repeated in this laboratory by Mr. E. H. Keiser, and the result first stated shown to be correct. Even when carbon monoxide is passed into a solution of hydrogen dioxide which is undergoing rapid decomposition by heat, no oxidation is effected. This result is just as inexplicable as the negative result obtained with heated ozone.

Further experiments are called for to determine whether there are not conditions under which hydrogen dioxide can oxidize carbon monoxide. Possibly the presence of one of the many substances known to have the power to decompose the dioxide may at the same time increase its oxidizing power.

March, 1882.

NOTE ON THE VOLUMETRIC ESTIMATION OF ZINC, BY TITRATION WITH POTASSIUM FERROCYANIDE.

By Robert W. Mahon.

According to a method previously described for the volumetric estimation of zinc, a standard solution of potassium ferrocyanide is obtained by titrating a solution of known strength of pure zinc, dissolved in hydrochloric acid. After each addition of potassium ferrocyanide a drop of the solution is tested with a drop of a solution of uranium acetate, to ascertain whether the whole of the zinc has been converted into ferrocyanide, and an excess of the potassium ferrocyanide added. As soon as an excess of potassium ferrocyanide is added, a brown spot is obtained by bringing a drop of the solution in contact with a drop of uranium acetate solution. For the

[1] Berichte der deutschen chemischen Gesellschaft, **15**, 222. [2] Ibid. **9**, 1876.

determination of zinc in its ores, they are dissolved in nitric and hydrochloric acids; and those metals whose sulphides are formed in acid solution are precipitated by sulphuretted hydrogen. After filtering, the iron is oxidized with nitric acid, and precipitated by addition of ammonium hydrate in excess, the zinc remaining in solution. The ammoniacal filtrate is made slightly acid, with hydrochloric acid, and, in the absence of manganese, is now ready for titration. In the case of Franklinite and other zinc ores containing manganese, this method for the estimation of zinc is not as easy of application as when manganese is not associated with zinc in the ore.

In the original paper describing the method, Fahlberg[1] directs that, after the separation of iron by excess of ammonia, the ammoniacal filtrate be made acid with excess of hydrochloric acid, and that the titration be made into this acid solution. The statement is made that the presence of manganese will not interfere with this titration. This statement I find to be erroneous. Both the manganese and zinc will be precipitated, even in a solution acid with hydrochloric acid. And, moreover, it is not possible to make the solution sufficiently acid to prevent such precipitation. When to a very dilute solution of a salt of manganese, in pure water, potassium ferrocyanide is added, the manganese is not at once precipitated. If ammonium chloride is present (the condition in the actual analysis), the precipitation will be more nearly instantaneous. When the quantity of manganese is considerable, the precipitation will occur at once, even in the absence of ammonium chloride.

The presence of manganese is then not allowable, even in small quantities, in the solution with zinc, where zinc is to be estimated by titration with potassium ferrocyanide. No way of precipitating manganese and leaving zinc in solution presents itself, as any precipitation of manganese by oxidation would necessarily carry down considerable quantities of zinc with it; such a precipitation, for example, as that of the oxides of manganese out of the solution of the acetate by addition of bromine water. This method for the separation of manganese and zinc, although frequently employed, is not permissible, as the precipitated oxides of manganese will carry down considerable quantities of zinc with them.

[1] Zeitschrift für analytische Chemie, **13**, 379.

In order to get a solution for titration when manganese and zinc are associated in an ore, it is necessary to precipitate the zinc as sulphide out of the solution strongly acid with acetic acid by sulphuretted hydrogen, and to redissolve this precipitate in hydrochloric acid.

Dr. Fahlberg informs me that, since his communication above referred to, he has also observed the precipitation of manganese by potassium ferrocyanide in hydrochloric acid solution.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY, March, 1882.

REVIEWS AND REPORTS.

REPORT ON ANALYTICAL CHEMISTRY.

ARSENIC.—E. Lyttkens,[1] director of the Chemical Station at Halmstad, has made some interesting statements regarding the very frequent presence of arsenic in prints, carpets, shades, etc. Within two and a half years (1878, 1879 and the first half of 1880) 1704 samples of these materials were examined at the station, and 23.3 per cent. found to contain arsenic. In each of these cases the test was made with 150 square centimeters of the material; but a Swedish law, taking effect on the 1st of July, 1880, prescribes that materials shall be regarded as containing arsenic when "a black, or brown-black, partially indistinct arsenic mirror can be obtained in a tube 1.5 to 2 mm. in diameter from 440 square centimeters of printed, or 220 square centimeters of dyed samples." During the three following months 151 samples in the quantities prescribed by the law were examined, and 34.4 per cent. found to contain arsenic. It was found in prints of all colors. In the case of dyed materials, samples having brown and red colors; in the case of carpets, those having yellowish-brown and gray colors yielded it most frequently.

The method of examination employed consisted of the following steps: Oxidation of the sample by means of chlorate of potassium and dilute sulphuric acid; addition of sulphite of sodium to reduce any arsenic acid that may have formed; filtration; precipitation of the arsenic by sulphide of hydrogen; filtration

[1] Versuchs-Stationen, **26**, 305.

after 12 hours; solution of the precipitate in warm carbonate of ammonium; evaporation of the solution to dryness; oxidation of the residue by means of chlorate of potassium and dilute sulphuric acid; evaporation to decompose and expel chlorine compounds; and, finally, reduction in Marsh's apparatus.

To obtain the arsenic mirror from arsenious oxide or the sulphides of arsenic, Ch. Brame[1] heats the material with oxide of barium. A portion of the arsenic is liberated and forms a mirror, while the remainder is oxidized and unites with the barium. The presence of arsenic acid in the residue is demonstrated by dissolving in nitric acid and adding nitrate of silver. Similar but less striking results are obtained by using the oxide of calcium, potassium or sodium. Realgar and orpiment when treated in this way yield mirrors, but less easily than arsenious oxide. In the case of orpiment there is deflagration. If the mirror is treated with chlorine and the product exposed to atmospheric moisture, arsenic acid is formed, and its presence may be verified by means of nitrate of silver.

To avoid the well-known danger of reduction when arseniate of ammonium-magnesium is heated for the purpose of converting it into pyroarseniate of magnesium, F. Reichel[2] recommends moistening the precipitate with nitric acid.

W. Fresenius[3] has subjected the Fresenius-Babo[4] method of detecting arsenic to a critical examination and found that, when it is executed in exact accordance with the directions of its authors, it fully justifies all the claims which were made for it by them. The immediate occasion of the investigation was a description of the method in a much modified form in the latest edition of Graham-Otto's Inorganic Chemistry, the modifications relating in part to details which were especially emphasized in the original article as essential. In order to ascertain when and how the various modifications originated, all accessible works assuming to describe the method were compared. This examination led to the remarkable discovery that only four of these works—those of R. Fresenius, H. Will, Gorup-Besanez and Ph. Th. Büchner, give the method in its original and correct form. Further investigation revealed the fact that the modifications were first proposed in the various editions of Graham-Otto or of Otto's work on the detection of poisons, and that these works, rather than the original article, had been used as sources of information by those in whose books the method is incorrectly described. It appeared, furthermore, that opinions regarding the method had become unfavorable in proportion to the extent of its modification from the original form.

SILICON.—W. Hempel[5] recommends fusion with the subnitrate of bismuth as an effective method of decomposing silicates. 0.5 gram of the silicate is mixed with 10 grams of the bismuth compound and

[1] Comptes Rendus, **92**, 188.
[2] Zeitsch. für analyt. Chemie, 1881, 522.
[3] Zeitsch. für analyt. Chemie, 1881, 496.
[4] Zeitsch. für analyt. Chemie, 1881, 89.
[5] Liebig's Annalen, **49**, 287.

the mixture gently heated until the evolution of oxide of nitrogen fumes ceases. The temperature is then raised until the mass fuses, and the heating afterwards continued for about ten minutes. The molten material is poured into a platinum dish floating upon cold water, and after cooling, treated with hydrochloric acid. The solution is then evaporated to dryness, the residue treated with hydrochloric acid, and the silica separated by filtering and washing with acid. The bismuth is then removed by diluting with water and treating the filtrate from the oxychloride with sulphide of hydrogen.

M. W. Iles[1] recommends for the same purpose, especially for the decomposition of slags containing lead, fusion with potassium hydroxide in silver crucibles. W. Bettel[2] advocates the use of gold-lined platinum crucibles for such fusions with potassium hydroxide.

CARBON.—A. Muntz and E. Aubin[3] propose what appears to be an excellent method for the collection, and preservation for future estimation, of the carbonic acid of the air. For this purpose glass tubes, drawn out at both ends and containing pumice-stone saturated with caustic potassa, which is free from carbonate, are sealed before the blowpipe. The tubes thus prepared at the laboratory are opened at the place where the air is to be tested, a measured volume of air aspirated through them, and again sealed. Whenever it is desired to determine the carbonic acid thus collected, one end of the glass tube containing it is placed in connection with a mercury air-pump and eudiometer, and after a partial vacuum has been established, dilute sulphuric acid is admitted at the other end. The carbonic acid is then estimated by absorption.

ELECTROLYTIC DETERMINATIONS AND SEPARATIONS.—A Classen and M. A. von Reis[4] have found that accurate quantitative determinations and separations can be effected in the case of quite a number of metals by subjecting their double alkaline oxalates to electrolysis. The metals which can be thus determined and separated either from each other or from other elements are cobalt, nickel, iron, zinc, manganese, bismuth, lead, copper, cadmium, tin and antimony.

1. *Cobalt.*—The solution is treated with sufficient oxalate of ammonium to form the double salt; heated; three or four grams of solid oxalate ammonium added; and while still hot, subjected to electrolysis. When the metal has been completely precipitated, the positive electrode is removed, the liquid poured off, and the precipitate washed—first with water, then with alcohol, and finally with absolute ether. The arrangement of electrodes preferred by the authors consists of a flat platinum dish to contain the liquid and receive the deposit, and a platinum disk attached at its center to a stout platinum wire. A battery of two Bunsen's cells is recommended.

[1] Chemical News, **43**, 78.
[2] Chemical News, **43**, 94.
[3] Comptes Rendus, **92**, 247.
[4] Berichte der deutsch. chem. Gesellschaft, **14**, 1622.

2. *Nickel.*—The precipitation is effected in precisely the same manner as that of cobalt.

3. *Iron* is quickly and completely precipitated—provided a sufficient excess of the oxalate of ammonium is added—as a brilliant, steel-gray, perfectly adherent coating, which may be exposed to the air for several days without undergoing perceptible oxidation.

4. *Zinc* precipitates as satisfactorily as the preceding metals. The deposit cannot, however, be readily removed from the platinum by means of acids. It is necessary to ignite the residue which does not dissolve, and then repeat the treatment with an acid.

5. *Manganese,* if oxalate of potassium instead of the ammonium salt is used, is completely precipitated upon the positive pole as superoxide, but the precipitate adheres so loosely that it must be collected upon a filter and determined as tetroxide. It is not completely precipitated from solutions containing oxalate of ammonium.

6. *Bismuth* can be precipitated from the oxalate of ammonium solution; and, if a large platinum dish is used, the deposit is sufficiently compact to admit of washing.

7. *Lead* is precipitated, but is oxidized so rapidly in contact with the air that its determination by this method cannot be recommended.

8. *Copper* is readily precipitated from solutions containing a considerable excess of the oxalate of ammonium, provided a strong current (one equivalent to 330 cc. of electrolytic gas per hour) is employed.

9. *Cadmium* precipitates, and the deposit adheres well enough to admit of careful washing.

10. *Tin* can be deposited either from the double ammonium oxalate or from its solution in hydrochloric acid. There is, however, some difficulty in removing the deposit from the platinum.

11. *Antimony* can be precipitated from the double potassium oxalate or its solution in hydrochloric acid, but not in compact condition. The addition of an alkaline tartrate gives a firmly adhering deposit, but greatly retards the precipitation. Good results are, however, obtained by precipitating from the double sulphide of antimony and ammonium. The solution, which may contain an excess of hydrochloric acid, is saturated with sulphide of hydrogen, neutralized with ammonia, and then treated with an excess of sulphide of ammonium. From this solution the antimony separates as a fine, light-gray coating, which adheres firmly to the platinum, if the precipitation is not too rapid.

12. *Separation of Iron and Manganese.*—The solution is prepared in the same manner as for the precipitation of cobalt, nickel or iron, by adding an excess of oxalate of ammonium, heating, and then dissolving in it 3 or 4 grams of the solid oxalate. The iron is completely precipitated, and perfectly separated from the manganese, provided the proportion of the latter is not too large. If the quantity of manganese is twice that of the iron, or greater, the separation is imperfect. The difficulty can be remedied by adding

oxalic acid (without interrupting the current) until the manganese precipitate is dissolved. There precipitation of the manganese is attended with a perfect separation of the two metals.

13. *Separation of Iron and Aluminium.*—The neutral or slightly acid solution is treated with an excess of ammonium oxalate, and 2 or 3 grams of the solid oxalate added for every 0.100 gram of oxides of iron and aluminium. It is then heated, and while hot subjected to electrolysis. The iron precipitates completely; but the aluminium remains in solution until the quantity of carbonate of ammonium, formed by the decomposition of the oxalate, exceeds that of the remaining oxalate of ammonium, when the precipitation of aluminium as hydroxide begins. The solution is tested from time to time for iron, and the current interrupted as soon as possible after the last traces of it have disappeared. The separation is complete when the quantity of aluminium does not exceed that of the iron, otherwise the precipitate of aluminium hydroxide must be dissolved with oxalic acid, as in the case of the separation of iron and manganese, and then allowed to reform.

In a separate publication entitled "Quantitative Analyse auf electrolytischem Wege," Classen gives detailed directions for the application of his method of electrolysis to the analysis of nearly fifty alloys, ores and metallurgical products.

METALS AND ALKALIES.—W. Bachmeyer[1] recommends a solution of tannin as a sensitive reagent for caustic alkalies. A distinct red or reddish-brown color, which is transformed after a time into a dirty green, is produced. By means of this reaction one part of a caustic alkali in 1,000,000 parts of water can be detected. It also serves for the detection of minute quantities of the neutral carbonates of the alkalies. The other salts of the alkalies produce no visible effect on the solution of tannin.

According to L. L. de Koninck[2] the double nitrite of cobalt and sodium, prepared by adding the chloride of cobalt and acetic acid to a 10 per cent. solution of sodium nitrite, is a more sensitive reagent for the detection of potassium than the chloride of platinum. It gives an immediate precipitate in a solution containing one per cent. of potassium chloride, and a precipitate after some time in a solution which is ten times as dilute.

In addition to the numerous impurities—such as chlorides, sulphates, nitrites, cyanides, sulphocyanides, &c., which have been found in the sodium hydroxide of commerce since its manufacture directly from the red lye of the soda process has been introduced, E. Donath[3] has detected arsenic and vanadium. These impurities, he states, must have been introduced through the sulphuric acid employed in the process.

To separate lithium from large quantities of potassium and sodium, W. F. Gintl[4] makes use of the difference in solubility of their chlorides in strong hydrochloric acid. The mixture

[1] Zeitschrift für analyt. Chemie, 1881, 234.
[2] Zeitschrift für analyt. Chemie, 1881, 390
[3] Dingler's polytech. Journal, **240**, 318.
[4] Dingler's polytech. Journal, **240**, 83.

of dried chlorides is digested for two hours upon the water-bath with four or five volumes of strong hydrochloric acid, with replacement from time to time of the evaporated acid. After cooling, the solution is decanted through a filter of glass wool which has been thoroughly washed with strong acid. The same treatment is twice repeated with the residue, which is then brought upon the filter and washed with strong hydrochloric acid until the filtrate is free from lithium. The filtrate is evaporated to one-twentieth of its volume, treated with three volumes of strong hydrochloric acid, and filtered. The residue is then washed, as before, with strong hydrochloric acid. The final filtrate contains all the lithium and very little potassium or sodium.

H. N. MORSE.

ON A POSSIBLE NEW KIND OF ISOMERISM.

As is well known, isomerism in the usual sense has nothing to do with the kind of union existing between the atoms which form a molecule. If, in a given compound, it can be shown what connections exists between the atoms; if it can be shown that this carbon atom is in union with that hydrogen, and this oxygen atom with that carbon atom, and so on until all the connections are pointed out, then we say the structure of the compound is determined; and, in an isomeric compound, the connections between the atoms must be different, or, what is the same thing, different atoms must be united.

A second kind of isomerism, according to the hypothesis of Le Bel and Van't Hoff, is possible in two compounds in which the same atomic connections exist. In any compound in which there is a carbon atom, four bonds of which are satisfied with four unlike atoms or groups, we can conceive these four groups arranged in space in two ways. Imagining the carbon atom to be situated in the centre of a tetrahedron, and the four unlike groups or atoms at the four angles of the tetrahedron, then the groups may be arranged in such a way as to form one of the two possible tetrahedra, or in such a way as to give the complementary tetrahedron. The isomerism is here due not to different connections, but to different arrangement of the atoms in space around the carbon atom.

A third kind of isomerism is suggested by some formulas in common use. We speak of single and double linkage and represent these conditions by single and double lines. We can conceive of a kind of isomerism represented by the two formulas $CH_2—CH_2$ and $CH_2{=}CH_2$. In such a case the isomerism would be due to a difference in the kind of union existing between the carbon atoms. No such cases have thus far been observed.

Whether they are possible or not is not known, nor is it by any means certain that there is such a condition as that which is called double linkage, if by the expression is meant what the formula implies—union by twice the force that operates in single linkage.

Some investigations of W. H. PERKIN which have been carried on for the past seven years seem to lead to the conclusion that isomerism may be due to a cause hitherto not considered. This new kind of isomerism is the simplest, and it increases apparently the number of possibilities to an infinite extent. It is due to *differences in the distances between atoms.* Accepting the suggestion of Perkin, we might have isomerides of every known compound. Thus there might be a sodium chloride Na—Cl in which the atoms are near together, and another Na——Cl in which the atoms are more widely separated; and indeed, carrying out the idea, we might apparently have an infinite number of varieties of every chemical compound. Judging from the facts in our possession, it is not probable, however, that the above kind of isomerism is common, and for this we may be thankful. A brief account of Perkin's papers is here given.

Some years ago he showed that when the sodium compound of salicylic aldehyde and acetic anhydride are brought together, coumarin, a substance occurring in nature in the Tonka bean, is formed. Since that time several attempts have been made to explain the reaction, and it is in connection with this work that the observations under consideration were made. As regards the reaction involved in the formation of coumarin, it may be said that it is somewhat like that which takes place between benzoic aldehyde and acetic anhydride, resulting in the formation of cinnamic acid. The two reactions are represented thus:

$$2C_6H_4\begin{<}{OH \atop COH}+\begin{>}{CH_3CO \atop CH_3CO}O=3H_2O+2C_6H_4\begin{<}{OCO \atop C_2H_2}$$

Salicylic aldehyde. Acetic anhydride. Coumarin.

$$2C_6H_5COH+\begin{>}{CH_3CO \atop CH_3CO}O=H_2O+2C_6H_5.C_2H_2.CO_2H$$

Benzoic aldehyde. Acet. anhyd. Cinnamic acid.

Coumarin is the anhydride of coumaric acid, the formula of which is $C_6H_4\begin{<}{OH \atop C_2H_2.CO_2H}$.

When methylsalicylic aldehyde is treated with acetic anhydride this reaction takes place:

$$2C_6H_4\begin{<}{OCH_3 \atop COH}+\begin{>}{CH_3CO \atop CH_3CO}O=H_2O+2C_6H_4\begin{<}{OCH_3 \atop C_2H_2CO_2H}.$$

The change in this case is confined to the aldehyde group, the group OCH_3 remaining unchanged. The product is called *β-methylorthoxyphenylacrylic acid.*

Now when the sodium derivative of coumarin, obtained by boiling coumarin with sodium hydroxide, was treated with enough methyl iodide to combine with *half* the sodium, and the resulting compound treated with hydrochloric acid, a new acid was obtained, the analysis of which showed the formula to be $C_{10}H_{10}O_3$. It is identical in composition with the β-acid above mentioned, and is called *α-methylorthoxyphenylacrylic acid.* The two isomeric substances differ very markedly in their properties. Assuming the sodium derivative of coumarin to have the constitution expressed by the formula $C_6H_4<^{ONa}_{C_3H_2}CO_2Na$, by treatment with enough methyl iodide to combine with half the sodium we would obtain either $C_6H_4<^{ONa}_{C_3H_2.CO_2CH_3}$ or $C_6H_4<^{OCH_3}_{C_2H_2CO_2Na}$; and from these compounds by treatment with hydrochloric acid either $C_6H_4<^{OH}_{C_3H_2.CO_2CH_3}$ or $C_6H_4<^{OCH_3}_{C_2H_2CO_2H}$. It might be thought at first that the difference between the α- and β- acids consists in the fact that in one the methyl group is in the phenol hydroxyl, and in the other in the carboxyl. That this is not so is proved by a careful consideration of all the facts. In the course of an elaborate and interesting argument Perkin shows: (1) That both acids have the formula $C_6H_4<^{OCH_3}_{C_3H_2.CO_2H}$; (2) that both are ortho compounds; and (3) that the group C_3H_2 is the same in both. Compounds corresponding to the α- and β-acids have been obtained from homologues of coumarin, as from propionic and butyric coumarins.

Summing up all the evidence at command, the conclusion is reached that "this isomerism cannot be explained by any ordinary kind of chemical constitutional formula we have at present." Comparing the physical properties of the corresponding members of the two series of isomeric compounds, we find: that the boiling points of the α-compounds are always the lower; that the densities of the α-compounds are lower than those of the β-compounds; that "the magnetic rotary power of the methylic α- and β-methylorthoxyphenylacrylates shows a difference in the same direction, the α giving a lower result than the β, considerably greater than the variations of the densities would account for."

"*These facts would seem to indicate that in the α- compounds the groups, or some of them, contained in the molecules are farther apart than in the β- compounds.*"

"There is one point connected with this matter of isomerism worthy of note, and that is, that the changes of condition which these bodies undergo are always associated with *dehydration* and *rehydration.* Thus β-coumaric acid on losing the elements of a molecule of water becomes coumarin. This when hydrated does not go back to β-coumaric acid, but to its unstable isomeride α-coumaric acid, and it is not until this (or rather its salt) is strongly

heated that the original acid is reproduced. The difference in stability between α and β compounds is also seen to be in connection with the hydroxyl. These remarks also apply to the cases of maleic and fumaric acids, and citraconic and mesaconic acids, where we find the formation of maleic or citraconic resulting from the removal of a molecule of water from fumaric or mesaconic acids and rehydration of the product.

"It may be remarked in passing, that nearly all the bodies which are now called physical isomerides are hydroxylized products, and those containing the largest number of hydroxyls have the largest number of these isomerides, as in the case of the carbohydrates."

In the last paper published in connection with this line of investigation, Perkin gives an account of experiments on citraconic and mesaconic ethers, and maleic and fumaric acids, and arrives at the interesting conclusion that "there is but one anhydride for maleic and fumaric acids, one anhydride for citraconic and mesaconic acids, and one anhydride for α- and β-coumaric acids."

He concludes that the isomerism of these acids can be due to nothing else than a difference in the relationship of the hydroxyl to the radicals.—(*Journal of the Chem. Soc.*, 1877, p. 388–427; 1881, p. 409–452; 1881, p. 554–562).

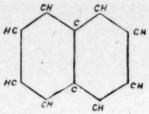
Quinoline and its Recent Synthetical Formation.

Although this substance has long been known to chemists, the interest attaching to it has been, until comparatively recently, purely scientific rather than practical. Skraup's demonstration, however, that it can be synthetically prepared on a scale sufficiently large for commercial purposes, together with the fact that it bears a close resemblance to quinine in physiological effects, and that it has already come into use as a remedial agent under the name of "artificial quinine," has brought it into prominence.

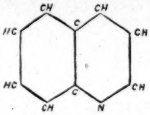
Quinoline belongs to the class of carbon compounds known as the "alkaloids," a group of bodies so called on account of their basic properties, *i. e.* their power of combining with acids to form salts. All alkaloids contain carbon, hydrogen and nitrogen; most of them contain, in addition to these three elements, oxygen. They resemble in their general properties the alkalies, but are more strictly analogous to ammonia than to the so-called fixed alkalies, as their combination with acids is direct without the formation of water. Quinoline forms the first member of an homologous series of alkaloids known as the *quinoline series*, the members of which correspond to the general formula $C_nH_{2n-11}N$, the formula of quinoline being C_9H_7N. The best known of the remaining members of the series are lepidine, $C_{10}H_9N$, and cryptidine, $C_{11}H_{11}N$.

This series of alkaloids may be obtained by the distillation of several alkaloids which occur in nature, *i. e.* by the distillation of quinine, cinchonine, strychnine. Quinoline may also be obtained from coal-tar, but the labor involved in this method is very great. As a result of the preparation of this substance on the large scale, a vigorous effort is at present being made to introduce it into medicine, on account of its agreeable character and cheapness, as a substitute for quinine. It will not, therefore, be out of place to present a short history of quinoline, and of the various syntheses made, all of which have tended to throw light upon the structure of the body, but which, owing to the small yields obtained, are, with the exception of Skraup's method, only of scientific interest.

Körner's hypothesis of the structure of quinoline was a valuable one, in that it suggested to other investigators reactions by which it could be produced. This hypothesis assumes that quinoline is naphthalene in which a CH group is replaced by an atom of nitrogen, thus naphthalene is represented by the formula



and quinoline by the formula



Baeyer's synthesis[1] of quinoline from hydrocarbostyril, $C_6H_4<\begin{matrix}NH\\C_2H_4.CO\end{matrix}$, furnished the experimental basis for Körner's formula. König's synthesis[2] from allylaniline also furnishes some support for the same formula.

Skraup's synthesis[3] was suggested by a consideration of Graebe's work on alizarin blue. Graebe found that alizarin blue can be produced from nitroalizarin and glycerin, these substances acting upon each other under the proper conditions according to the following equation:

$$\underset{\text{Nitroalizarin.}}{C_{14}H_7(NO_2)O_4} + \underset{\text{Glycerin.}}{C_3H_8O_3} = \underset{\text{Alizarin blue.}}{C_{17}H_9NO_4} + 3H_2O + O_2.$$

Graebe believed that alizarin blue is a substance allied in chemical structure to quinoline. Skraup then assumed that, if Graebe's

[1] Berichte der deutschen chemischen Gesellschaft, **12**, 1320. [2] Ibid. **12**, 453.
[3] Monatshefte für Chemie, Feb. 1881.

opinion were true, the formation of quinoline from nitrobenzene should result by a reaction analogous to the above in which nitro-alizarine is replaced by nitrobenzene. He also assumed that the homologues of quinoline should in like manner be formed by the action of glycerin upon substituted nitrobenzenes. These opinions were substantiated by experiment. In the above equation it is noticeable that free oxygen is evolved, and to the action of this element both Graebe and Skraup ascribed the formation, together with alizarin blue, of an undesirable brown-colored by-product. To avoid this destructive action of oxygen on the products, the presence of a reducing agent was considered necessary, and, in the case of the formation of quinoline, Skraup regarded the amide compound, $C_6H_5NH_2$, *i. e.* aniline, corresponding to the nitro compound $C_6H_5NO_2$, as the agent best suited for reducing purposes.

The reaction analogous to the above, by which quinoline is formed, is as follows:

$$\underset{\text{Nitrobenzene.}}{C_6H_5NO_2}+\underset{\text{Glycerin.}}{C_3H_8O_3}=\underset{\text{Quinoline.}}{C_9H_7N}+3H_2O+O_2.$$

Skraup believed that a reaction would also take place directly between aniline and glycerin thus:

$$\underset{\text{Aniline.}}{C_6H_5NH_2}+\underset{\text{Glycerin.}}{C_3H_8O_3}=\underset{\text{Quinoline.}}{C_9H_7N}+3H_2O+H_2.$$

These two reactions may be expressed in one:

$$\underset{\text{Aniline.}}{2C_6H_7N}+\underset{\text{Nitrobenzene.}}{C_6H_5NO_2}+3\underset{\text{Glycerin.}}{C_3H_8O_3}=3C_9H_7N+11H_2O.$$

We see then that aniline has in this reaction a double function, *i. e.* it neutralizes the destructive effect of oxygen and also contributes directly to the formation of quinoline. This double function of aniline has been clearly substantiated by experiment. In the formation of quinoline by this method the presence of sulphuric acid is necessary as a dehydrating agent. Skraup gives the following directions for the process: 24 grams nitrobenzene, 38 grams aniline and 120 grams glycerin are mixed with 100 grams oil of vitriol in a 2 litre retort; the mass, which has become warm, is shaken up until the aniline sulphate is perfectly dissolved, and is then heated on a sand bath, a long inverted condenser being also employed. At the beginning, the operation must be carefully watched in order to regulate the action, which is violent. Full details of the process are given in Skraup's paper to which reference is above made. The yield in raw quinoline by this process is from 70 to 75 per cent. of the weight of the mixture of aniline and nitrobenzene, that is about 60 per cent. of the amount theoretically possible is obtained. Quinoline thus obtained agrees, according to Skraup, perfectly with that obtained from cinchoninic acid.

The physiological effects of quinoline have already been investigated to a considerable extent, experiments having originally been made upon animals, and later on human beings, both in health and in sickness. Donath has occupied himself with the study of quinoline in its physiological action, and has announced its similarity to quinine. Loewy has reported in the *Vienna Medical Press* a number of cases successfully treated by means of quinoline. Salkowsky, of St. Petersburg, also gives a favorable report. It is stated that none of the inconveniences attendant upon the use of quinine, such as dizziness, loss of hearing, etc., are noticed when quinoline is employed.

The evidence as to the value of quinoline as a curative agent must still, however, be considered as incomplete; but, owing to the importance of this question, a satisfactory solution will probably not long be wanting. W. C. D.

THE JOURNAL OF THE SOCIETY OF CHEMICAL INDUSTRY: A MONTHLY RECORD FOR ALL INTERESTED IN CHEMICAL MANUFACTURES. No. 1, Vol. I. January, 1882.

About a year ago the Society of Chemical Industry was inaugurated in England with these objects:

"To advance Applied Chemistry in all its branches.

"To promote the acquisition and practice of that species of knowledge which constitutes the profession of a Chemical Engineer.

"To enable all persons interested in Applied Chemistry to meet and to correspond; to facilitate the interchange of ideas respecting improvements in the various branches of chemical manufacture; and to publish and communicate information on such subjects."

Prof. Roscoe was elected president, and among the vice-presidents are Abel, Lowthian-Bell, Muspratt, Pattinson, Perkin, Siemens, Weldon, Williamson. Other distinguished names are found in the list of the members of the committee. With such men taking active part in the workings of the society it can not help being a success. The Society has now started a journal. Watson Smith of Owens College is the editor, acting under instructions from the publication committee, of which Prof. Roscoe is the chairman. The first number of the journal contains interesting matter, and if the standard is maintained, it will certainly be a valuable addition to the literature of Applied Chemistry. The principal contents of the number are: Professor Abel's address at the opening meeting of the Metropolitan Section of the Society; Specific Gravity Tables by Dr. Messel; Dynamic Theory of Manufacture of Sulphuric Acid, by F. Hunter; Society of German Alkali Makers: Report by Prof. Lunge; on Artificial Indigo, by Profs. H. E. Roscoe and A. Baeyer.

NOTES.

On Artificial Indigo.

Prof. Roscoe writes in *The Journal of the Society of Chemical Industry*, No. 1, Vol. I.: "As supplementing the information on this interesting subject contained in my lecture,[1] delivered at the Royal Institution in May last, I have now the pleasure of adding the following particulars of Professor Baeyer's observations on his visit to the manufactory of artificial indigo in November last. This shows that the production of artificial indigo is making progress; and I may add that the manufacture is being carried on up to the present day in the manner described by him. It appears, however, that the consumption of propiolic acid is at present limited to a few print works, whose chemists have successfully overcome the difficulties of its application. Let us hope that the great majority of English calico printers will soon follow in the wake of the pioneers. The important question referred to by Professor Baeyer in his letter, viz. that of finding a useful employment for para-nitro-cinnamic acid, now a waste product in the manufacture of propiolic acid—may possibly receive a solution from the recent researches of Otto Fischer on the synthesis of the rosaniline dyes, by means of para-nitro-benzaldehyde, a body obtained by the limited oxidation of para-nitro-cinnamic acid. Another point which requires attention is the loss of material incurred in the passage from propiolic acid to indigo. If this loss can be avoided, and if a use is found for the para acid, there seems no reason why indigo blue should not be itself obtained in course of time by Baeyer's reactions, particularly as cinnamic acid can now be made in any quantity, and at a very low price.

"That these researches are only the first steps in the production of colors from the indigo group of compounds is shown by the fact that Professor Baeyer, in February last, patented the production of another coloring matter, termed by him 'indoin.' This resembles indigo in color, and is obtained by the action of concentrated sulphuric acid upon ortho-nitro-phenyl-propiolic acid, when isatogenic acid is formed, and this is converted into the coloring matter by the action of ferrous sulphate. The soluble sulphurous acid compound of indoin is remarkable, and may become useful as a dye."

The following extracts from Professor Baeyer's letter will be of interest: "Propiolic acid is at this moment made at Ludwigshafen with the same degree of certainty as is attached to the preparation of any inorganic compound. . . . The first necessity in the technical preparation of propiolic acid is a cheap cinnamic acid. Your celebrated countryman, Perkin, was the first to make this acid by a simple reaction, viz. by heating bitter almond oil with

[1] See this Journal, **3**, 282.

acetic anhydride and acetate of soda. The Baden company simplified this reaction, as far as it can be simplified, and prepared cinnamic acid directly by fusing benzyl chloride with acetate of soda, and thus obtaining the acid without using either acetic anhydride or oil of bitter almonds. This reaction is carried on in large boilers fitted with mechanical stirrers, and gives a very satisfactory yield. Great difficulties were met with in nitrating cinnamic acid; but, thanks to the ability and patience of the chemists to the Baden company, these difficulties have been overcome, and a process has been found by which the operation can be conducted on any wished for scale, and with good results. I was amazed to see hundredweights of cinnamic acid undergoing the operation of treatment with nitric acid, for I remembered how difficult a task it was to work up a single pound in the laboratory. The preparation of ortho-nitro-cinnamic acid is carried out, first, by the conversion of cinnamic acid into its ethyl ether. The liquid ether is then allowed to run in a thin stream, together with the requisite quantity of a mixture of nitric and sulphuric acids, into a well-cooled vessel furnished with a stirring apparatus. The solid mixture of ortho and para-nitro-cinnamic ethers thus obtained is heated with alcohol, when the para-nitro-cinnamic ether remains undissolved, the ortho ether being dissolved, and deposited from the alcoholic solution in large yellowish crystals. This compound, on saponification, yields ortho-nitro-cinnamic acid. The conversion of this acid into ortho-nitro-phenyl-propiolic acid is carried out in two consecutive operations, both of which work well. The ortho acid is first acted on by bromine, by which means the dibromide is formed, and this is then dissolved in caustic-soda ley, when the soda salt of propiolic acid is formed. Propiolic acid itself is precipitated from the solution of the soda salt by means of an acid, and, after washing, it is sent to market as a paste. Artificial indigo is not itself manufactured in the works, the coloring matter being deposited by the printer himself in the fibre of the cloth from propiolic acid, as is aniline black from aniline. For this purpose a mixture of propiolic acid and xanthate of soda, to which a proper amount of thickening has been added, is printed on the cloth. The color makes its appearance on exposure to the air (ageing). It is found to be fast, and exhibits the characteristic tints of indigo in both light and dark shades.

"The series of operations necessary for passing from toluene to indigo blue are, as is seen, rather long, but each process works so regularly and well that the preparation of propiolic acid and its conversion into indigo blue can be carried out with perfect ease. The only serious imperfection in the process is the loss of 40 per cent. of the cinnamic acid in the form of para-nitro-cinnamic ether. This will, it is to be hoped, be overcome by the employment of the compound for some useful purpose. On my visit to Ludwigshafen last November, I found the manufacture of indigo in full activity—200 kilograms of propiolic acid paste, containing 25 per cent. of the dry acid, were produced every day, and this is sold at the price of 10 shillings the kilogram."

Levulose.

Levulose has for a long time been distinguished by the name of uncrystallizable sugar, and, although it has been the subject of much investigation, it has hitherto never been isolated in a satisfactory state of purity, and the physical properties which have been attributed to it have either been observed with very impure specimens of levulose, or, oftener, deduced from the differences between the properties of glucose and those of the mixture of glucose and levulose known by the name of inverted sugar.

JUNGFLEISCH and LEFRANC have now succeeded in preparing pure levulose in crystalline form and have studied its properties. Inuline was selected by them as the most advantageous starting point, from the fact that it yields levulose alone, by complete saccharification. A solution of inuline in water, containing several thousandths of sulphuric acid added in the form of titrated solution, was heated to 100° for one hour, and, after cooling, the sulphuric acid removed from the solution by the addition of an amount of titrated baryta-water equivalent to the amount of acid used. The solution was then decolorized with animal charcoal, filtered, and the filtrate evaporated upon the water-bath *in vacuo* to a syrupy consistence. The solution if now left to itself would retain the syrupy form indefinitely, and, on the other hand, if dessicated over sulphuric acid, would lose more or less water and be converted into a solid, vitreous, hygroscopic mass. The great difficulty consists, then, in the removal of water from the solution without the transformation of the levulose into dehydration products which very readily takes place. This was accomplished by treating the syrupy residue with cold absolute alcohol, which only dissolves a slight trace of the saccharine matter, but abstracts water as well as certain impurities. After several washings with absolute alcohol, the insoluble portion was placed in a carefully closed vessel and left to itself in a cool place. Gradually fine needle-shaped crystals analogous to crystals of mannite made their appearance, and finally the entire mass assumed crystalline form. This crystallization was found to be effected more rapidly and more surely if a crystal of levulose previously obtained be added to the solution.

In order to decide the question which has been several times discussed of late as to the identity of levulose from inuline with that of inverted sugar, levulose was prepared from inverted sugar by a modification of the method of Dubrunfaut. Pure crystallized levulosate of calcium was decomposed under water by means of oxalic acid, and the solution of levulose thus obtained treated as described above by evaporation to syrupy consistence and washing with absolute alcohol. Levulose obtained in this manner was found to be in every respect identical with that from inuline. There is then but one variety of levulose and the name of uncrystallizable sugar should no longer be applied to it.

Levulose crystallized from alcoholic solution consists of fine colorless silky needles, which sometimes attain the length of 10 mm. and which usually radiate from a central point forming spherical groups. When freed from mother-liquor and dried over sulphuric acid, their composition is represented by the formula $C_6H_{12}O_6$. When moistened with alcohol and exposed to the air, levulose is deliquescent, but when perfectly dry it is very slightly hygroscopic, and only increases from one to two per cent. in weight when exposed to the air for several days. It fuses at about 95°, and at 100° loses water gradually, yielding ether derivatives. As would be expected from the optical properties of inverted sugar, the rotatory power of levulose varies very rapidly with the temperature; it also varies in a still greater degree with the dilution of the solution. MM. Jungfleisch and Lefranc announce their intention of continuing their investigations of this subject.—(*Comptes rendus*, **93**, 54). R. D. C.

On a new Series of Bases derived from Morphine.

Since the transformation of morphine into codeine, an account of which has already been given, E. GRIMAUX has continued his investigations on morphine, and has succeeded in obtaining from it a new series of bases. When codeine or the sodium derivative of morphine is treated with methyl iodide, there is obtained, as has been shown, the iodomethylate of codeine, which possesses the properties of a quaternary iodide of ammonium. If now this be treated with silver oxide, there is obtained, not the corresponding hydrate of ammonium, but, by simple concentration on the water-bath, it is transformed into a solid and crystallizable tertiary base. This base is slightly soluble in water, easily soluble in alcohol and ether, and crystallizes from its alcoholic solution in brilliant needles which fuse at 118.5°. It is precipitated from its salts by potash and by ammonia, differing in this respect from codeine and codethyline, which ammonia does not precipitate. It gives with sulphuric acid a characteristic reaction. The concentrated acid colors it brown, then by the addition of a few drops of water it dissolves, forming a solution of intense blue-violet color. A further addition of water changes the color to clear red and then destroys it completely. This reaction is exactly like that given by cryptopine. The new base appears to be formed by the abstraction of a molecule of water from the quaternary hydrate of ammonium, and to constitute methocodeine, $C_{18}H_{20}NO_2(OCH_3)$, an isomer of codethyline, $C_{17}H_{18}NO_2(OC_2H_5)$. Claus has shown that by treatment with potash the quaternary iodides of ammonium derived from cinchonine and cinchonidine yield tertiary bases with loss of the elements of hydriodic acid in such a manner that the alcoholic group, at first in combination with nitrogen in the ammonium iodide, finally enters into combination with the hydrocarbon radical. It appeared to M. Grimaux that the formation of methocodeine,

being due to a reaction of the same class, should take place under the same conditions; and he found, in fact, that when iodomethylate of codeine was boiled with an aqueous solution of potash, methocodeine was produced. The yield, however, was much better with silver oxide, in which case the transformation takes place below 100°. In order to generalize this reaction, iodomethylate of codethyline was also prepared and treated with silver oxide and with potash, and by this means a tertiary crystallizable base obtained, fusing at 132°, resembling methocodeine, but less soluble in ether, and giving with sulphuric acid the same violet coloration. This base has not been analyzed as yet, but is in all probability methocodethyline, $C_{18}H_{21}NO_2(OC_2H_5)$. This is then a general reaction by means of which there can be obtained homologues of codeine containing new alcoholic groups, not in the phenol hydroxyl of the morphine, but in the hydrocarbon radical of the morphine itself. It is in this manner that methocodeine is, as has been said above, isomeric with codethyline:

Methocodeine.	Codethyline.
$C_{18}H_{20}NO_2(OCH_3)$	$C_{17}H_{18}NO_2(OC_2H_5)$.

—(*Comptes rendus*, **93**, 591). R. D. C.

On the Proportions of Carbonic Acid in the higher Regions of the Atmosphere.

A. MUNTZ and E. AUBIN have recently made determinations of the proportions of carbonic acid in the atmosphere both in the city of Paris and in the open country near Vincennes, the results of which agree with those of Reiset, showing that variations in the amount of carbonic acid only occur between very narrow limits and are due to local influences, and, in general, that the carbonic acid is uniformly distributed throughout the lower strata of the atmosphere. They have continued their investigations upon the subject, and have applied their method of analysis to the air of elevated regions. Additional interest is lent to this part of their work, from the fact that some recent investigations seem to indicate a decided diminution in the amount of carbonic acid in the air upon mountains. The method of analysis devised by them, and which has been found to be capable of giving extremely accurate results, consists essentially in drawing a measured volume of air through tubes filled with fragments of pumice-stone saturated with caustic potash. These tubes are sealed at both ends before the blowpipe, immediately at the close of each experiment, and the determination of the amount of carbonic acid absorbed may then be made in the laboratory after an indefinite time. The air was always drawn through metallic tubes from a distance of 8 to 10 metres to the windward side of the operator.

The point selected for carrying on the experiments was the summit of the Midi in the Pyrenees, at the altitude of 2877 metres

(9422 ft.) above the level of the sea. This is an isolated peak distant from any other elevated summit; the air circulating about it is generally that of the upper currents of the atmosphere; and the great velocity of the wind dismisses any suspicion of local influence. During the course of the experiments the direction of the wind and the state of the atmosphere varied frequently; nevertheless, the proportion of carbonic acid in the air was found to be constant, the mean of a large number of observations giving 2.86 parts by volume of carbonic acid to 10,000 parts of air. This agrees very closely with the figure found in the experiments upon the plain at Vincennes (2.85). For the sake of comparison, experiments were made in two valleys at the foot of the Pyrenees, one near Pierrefitte (altitude 507 m.) and the other near Luz (altitude 730 m.) At the first station the result obtained was 2.79 volumes of carbonic acid to 10,000 parts of air, and at the second 2.69, the latter determination being made in the midst of a luxuriant vegetation. All the results obtained agree closely with those found in the lower regions of the atmosphere, and also with those found by Reiset and by Schultze in very varied situations.

As a result of their investigations MM. Muntz and Aubin consider themselves justified in stating that carbonic acid is uniformly distributed throughout the atmosphere, and that their results confirm the statements made by Reiset upon the subject and the theories of Schloesing in reference to the circulation of carbonic acid upon the surface of the globe.—(*Comptes rendus*, **93**, 797).

R. D. C.

Transformation of Xanthine into Theobromine and Caffeïne.

Xanthine is obtained from uric acid by reduction, is a constituent of certain rare urinary calculi, and can be prepared from guanine, a constituent of guano. It has the formula $C_5H_4N_4O_2$, while guanine has the formula $C_5H_5N_5O$. The formula of caffeïne, the alkaloid of coffee and tea, is $C_8H_{10}N_4O_2$. Caffeïne is the methyl derivative of theobromine, an alkaloid found in the chocolate bean. The formula of theobromine is hence $C_7H_8N_4O_2$. On comparing the formula of xanthine $C_5H_4N_4O_2$ with that of theobromine $C_7H_8N_4O_2$, it appears possible that the latter may be the dimethyl derivative of the former. Strecker made this suggestion some years ago, but, though he made some experiments with the object of determining whether the relation exists or not, they gave only negative results. Emil Fischer, in continuing his investigations on caffeïne, has again attempted to transform xanthine into theobromine, and has been successful. The lead salt of xanthine, which is a crystalline precipitate, was treated with methyl iodide in a sealed tube for twelve hours at 100°. Complete transformation was effected. The chief product had all the properties of theobromine.

The theobromine thus obtained was transformed into caffeine by the usual method. It is thus shown that theobromine is dimethylxanthine; and that caffeine is trimethylxanthine. Thus a direct line of connection is established between the active principles of guano and of coffee and tea.—(*Berichte der deutschen chemischen Gesellschaft*, **15**, 453.) R. D. C.

On the Active Condition of Oxygen.

In an interesting article, MORITZ TRAUBE discusses the various opinions that have been advanced with reference to the remarkable change of oxygen from the ordinary passive condition to the active condition. He then, further, describes a number of experiments which he undertook with the object of determining whether, when hydrogen dioxide is formed in consequence of slow oxidation of metals in the presence of water and air, its formation is due to oxidation of water, as is commonly held, or to reduction of oxygen. He shows that in most cases the formation cannot be ascribed to an oxidation process; for experiment proves that, if substances which are easily oxidized are present, they are not oxidized under the circumstances which give rise to the formation of hydrogen dioxide. Thus, when zinc is shaken with water and air, hydrogen dioxide is formed; but if indigo-sulphuric acid, an easily oxidizable substance, is present in the water, it is not oxidized. Hence it is not probable that the water, which in general resists the action of oxidizing agents, is oxidized under these conditions. It is also shown that potassium nitrate is readily reduced when brought together with zinc, water, and air, hydrogen dioxide being formed at the same time. The action accompanying the formation of the dioxide is reduction; and, in all probability, the dioxide itself is formed by the addition of hydrogen directly to oxygen, and not by the addition of oxygen to water.

The remarks introductory to the paper are interesting and are here given: "Oxygen at the ordinary temperature is characterized by great passivity. While at high temperatures it burns up all organic substances without exception, at ordinary temperature it affects but very few of them. In the animal body, on the other hand, it becomes active, and now has the power of effecting oxidations at temperatures below 40° which it can otherwise effect only at red heat. Here it burns up all carbohydrates, fats, and albuminoids, forming carbon dioxide and water, the alkali salts of the plant acids forming alkali carbonates. Regarded from this standpoint, the adult animal, which neither loses nor gains in weight, plays the part of a catalytic body, which without suffering material change in composition, causes at low temperatures, by means of the oxygen of the air, the almost complete combustion of enormous quantities of food. But not only animal organisms have the power of rendering oxygen active; the same property, though to a much

less extent, is possessed by plants, or, in general, by all organisms down to and including bacteria and fungi. There does not exist an organism which is indifferent towards oxygen; which, when brought in contact with this gas, will not take it up and be at least partly converted into carbon dioxide. Upon this power is based the most important act connected with the life process, the chemical part of respiration with which the effecting of the most important phenomena of life is intimately associated.

"It was formerly assumed, in accordance with Liebig's view, that respiration serves only the purpose of keeping up the temperature of the body and that the oxidation processes only take place in the blood. Even J. R. Meyer was of the opinion that respiration only produces heat which is transformed into motion in the muscles, and that the blood is the real hearth of the organic combustion processes. I first pointed out, with conclusive reasons, that the real hearth of the respiratory processes is, not the blood, but the tissues of the body, above all the muscles; that the oxygen taken up in the lungs is set free in the capillaries of the body, enters as dissolved gas into the tissues of the individual organs; and that in this way each individual organ breathes independently at the expense of the free oxygen. It is only in consequence of this breathing that the individual organs are enabled to grow, to perform their functions, to yield secretions, and to generate the different forces which characterize them, as, for example, the force of the muscle, nerve force, &c.

"Thus, not only do organisms as a whole have the power to make oxygen active, but each of their organs, indeed each individual cell; or rather they contain substances which have this power. Hence the problem of active oxygen is in the highest degree important, as well for physiology as for chemistry.

"Oxygen can also be made active by a few processes which take place without the organism. Thus, as is well known, it is affected in a high degree by platinum and phosphorus. In the presence of finely divided platinum it oxidizes energetically at the ordinary temperature hydrogen and alcohol, substances towards which it is usually indifferent. But, although the phenomena in inanimate nature are much more accessible to experimental investigation than the more complicated phenomena of life, a satisfactory theory of the process has not yet been framed on an experimental basis. A number of hypotheses regarding the process in inanimate nature as well as in the organisms have been advanced."

The views of De la Rive, Liebig, Schönbein, and Brodie are then given, and finally reference is made to the view of Hoppe-Seyler, according to which "hydrogen in the nascent state has the power to split the molecule of oxygen, uniting with one atom of the molecule and thus setting free the other as *active* oxygen possessed of highly energetic oxidizing power. According to the view of the same author the life process in the animal body

resembles a case of decomposition accompanied by an evolution of hydrogen, and it is this nascent hydrogen which renders the oxygen taken up in respiration active."

He then speaks of an hypothesis advanced by himself in 1858. "According to this the oxygen is rendered active by *oxygen transferrers* (Sauerstoffüberträger). These are bodies which . . . have the power of giving up easily to other bodies the oxygen which they absorb and then again taking up oxygen immediately. This process may be followed readily when the oxygen transferrer is colored in oxidized condition and colorless when reduced.

"The ammoniacal solutions of copper salts, and indigo-carmine, are easily reduced by many bodies, as grape sugar, and then become colorless. If, however, they are in contact with oxygen, they take it up again and are changed back to their original condition, only to give it up to the sugar. This alternating reduction and oxidation continues until all the sugar is oxidized, while the oxygen transferrer itself (for example, the ammoniacal copper solution) appears unchanged at the end of the experiment. Thus small quantities of the transferrers can transform large quantities of bodies which of themselves can not take up oxygen. . . . In the different parts of the paper which are to appear these various hypotheses will be discussed in full."—(*Berichte der deutsch. chem. Gesell.* **15**, 659.)

Formation of Alloys by Pressure.

W. SPRING has shown that, when a mixture of bismuth filings, cadmium and tin in the proportions necessary for the formation of Wood's alloy, is subjected to a pressure of 7500 atmospheres, the mass thus obtained powdered and again subjected to the same pressure, a metallic block is formed which has all the physical properties of the alloy. Its specific gravity, color, hardness, brittleness, and fracture are the same; and when thrown into water heated to 70°, it melts at once. In like manner Rose's metal was made by subjecting the proper mixture of lead, bismuth and tin to high pressure. If zinc and copper filings are repeatedly subjected to pressure, a mass resembling brass is finally obtained.—(*Berichte der deutsch. chem. Gesell.* **15**, 595.)

On the Conduct of Nitrogen Tetroxide towards Sulphuric Acid.

Lasne and Benker have recently taken out a patent in France for an invention having reference to the improvement of the processes involved in the manufacture of sulphuric acid. The improvement consists in introducing sulphurous acid and steam into the gases which enter the Gay-Lussac tower, so as to secure the reduction of all the nitrogen tetroxide N_2O_4, to the trioxide N_2O_3, and the formation of nitroxylsulphuric acid, $SO_2(OH)(ONO)$.

The object is to prevent loss of nitrogen in the form of the tetroxide. G. LUNGE now calls attention to the fact that the invention is based on a wrong conception of the conduct of nitrogen tetroxide towards sulphuric acid; that the tetroxide is readily and completely absorbed by sulphuric acid of 1.71 specific gravity, the weakest acid ever used in the Gay-Lussac tower; and that the acid acts upon the tetroxide, giving rise to the formation of nitroxylsulphuric acid and nitric acid, according to the equation:

$$N_2O_4 + SO_2(OH)_2 = SO_2(OH)ONO + NO_3H.$$

If, then, in the process of Lasne and Benker the introduction of sulphurous acid is of any value, the reason for this is certainly not what the inventors think it is. There is some doubt concerning the advantages of the process, as the statements of the manufacturers in regard to it are conflicting.—(*Berichte der deutsch. chem. Gesellschaft*, **15**, 488.)

The Atomic Weights of Lanthanum and Didymium.

The atomic weights of lanthanum and didymium have been redetermined by Brauner.[1] To lanthanum, without giving any details, he assigns the value 138.88. By converting didymium oxide into the sulphate, he found the following percentages of the former corresponding to the latter:

58.676
58.681
58.685

The mean is 58.681, for which the probable error is ±.0035.

If O = 16 and S = 32.074, this mean gives Di = 146.58.

If H = 1 and O = 15.96, this mean gives Di = 146.18.

In my recent recalculation of the atomic weights I found O = 15.9633, ±.0035, and S = 31.964, ±.012. Upon the basis of these values Brauner's data give Di = 146.210, ±.035.

It is worth while to compare Brauner's results with those of Cleve, which were obtained by the same method. Reckoned with SO_3 = 80, we have the following figures:

From Cleve's data . . .	Di = 147.021
From Brauner's data . . .	Di = 146.423
Difference,	0.598

It is plain that additional determinations are still needed.

F. W. CLARKE.

[1] Ber. d. deutsch. chem. Gesell. **15**, 109.